

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

APPENDICES

FOR THE

Report for the Application
and Ambient Air Monitoring
of Ethoprop in Siskiyou County

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Project No. C98-005 (Application)
C98-006 (Ambient)

Date: December 16 , 1998

APPENDIX I
SAMPLING PROTOCOL



M. Rooney
Secretary for
Environmental
Protection

Air Resources Board

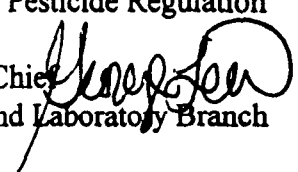
John D. Dunlap, III, Chairman
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Pete Wilson
Governor

MEMORANDUM

TO: Douglas Y. Okumura, Chief
Environmental Monitoring and Pest
Management Branch
Department of Pesticide Regulation

FROM: George Lew, Chief 
Engineering and Laboratory Branch

DATE: April 27, 1998

SUBJECT: FINAL PROTOCOL FOR THE 1998 ETHOPROP AIR MONITORING IN
SISKIYOU COUNTY

Attached is the final protocol, "Protocol for the Application and Ambient Air Monitoring of Ethoprop in Siskiyou County During Spring, 1998."

If you or your staff have questions or need further information, please contact me at (916) 263-1630 or Mr. Kevin Mongar at (916) 263-2063.

Attachment

cc: Ray Menebroker, Chief (w/Attachment)
Project Assessment Branch
Stationary Source Division

James R. Massey, Jr.
Siskiyou County
Agricultural Commissioner

Patrick Griffin
Siskiyou County Air Pollution Control Officer

bcc: Bill Loscutoff, MLD
Peter Venturini, SSD

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

**Protocol for the Application and Ambient
Air Monitoring of Ethoprop
In Siskiyou County During Spring, 1998**


Engineering and Laboratory Branch
Monitoring and Laboratory Division

Project No.
C98-005 Application
C98- 006 Ambient

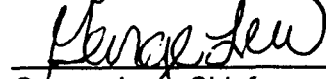
Date: April 15, 1998

APPROVED:

Kevin Mongar, Project Engineer



Cynthia L. Castronovo, Manager
Testing Section



George Lew, Chief
Engineering and Laboratory Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for the Application and Ambient
Air Monitoring of Ethoprop
In Siskiyou County During Spring, 1998

I. Introduction

At the request (July 24, 1997, Memorandum from Sanders to Lew) of the California Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide ethoprop in Siskiyou County over a six week ambient monitoring program and over a three day application monitoring program. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Monitoring is being conducted to coincide with the use of ethoprop as an insecticide on potatoes.

The draft method development results and "Standard Operating Procedures for the Analysis of Ethoprop in Ambient Air" are included as Attachment I.

II. Chemical Properties of Ethoprop

The following information on the physical/chemical properties of ethoprop (O-Ethyl S,S-dipropyl phosphorodithioate) was obtained from the July 24, 1997 memorandum "Use Information and Air Monitoring Recommendation for the Pesticide Active Ingredient Ethoprop".

Pure ethoprop (CAS:13194-48-4) exists as a clear, pale yellow liquid.. Ethoprop has a molecular formula of $C_8H_{19}O_2PS_2$, and a molecular weight of 242.33 g/mole. It has a water solubility of 700 mg/L at 20 °C, a Henry's Constant of 1.59×10^{-7} atm·m³/mol at 20-25 °C, and a vapor pressure of 3.49×10^{-4} mm Hg (46.5 mPa) at 20 °C. Ethoprop is miscible with acetone, *n*-hexane and xylene.

The reported half-lives in jumus-containing soil (pH 4.5) and a sandy loam (pH 7.2-7.3) were 87 and 14-28 days, respectively. Accelerated transformation of ethoprop after repeated soil applications was reported. When heated to decomposition, ethoprop emits toxic phosphorous and sulfur dioxide fumes.

The acute oral LD₅₀ of ethoprop for rats is 262 mg/kg. The LC₅₀ (96 hour) for rainbow trout is 13.8 mg/L, 2.1 mg/L for bluegill sunfish, and 13.6 mg/L for goldfish. Ethoprop entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984) based on potential combined oncogenicity and chronic toxicity and mutagenic effects.

III. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-2 resin. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest (dry ice) or freezer

until desorbed with 2.5 ml of ethyl acetate. The flow rate of 3 Lpm will be accurately measured and the sampling system operated continuously with the exact operating interval noted. The resin tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during application monitoring sampling periods and 1.5 meters above roof tops for the ambient monitoring. At the end of each sampling period, the tubes will be capped and placed in culture tubes with an identification label affixed. Subsequent to sampling, the sample tubes will be transported on dry ice, as soon as reasonably possible, to the ARB Monitoring and Laboratory Division, Testing Section laboratory for analysis. The samples will be stored in the freezer or extracted/analyzed immediately.

A sketch of the sampling apparatus is shown in Figure 1. Calibrated rotameters will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling cartridges installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data.

Ambient Monitoring

The use patterns for ethoprop suggest that monitoring should occur in Siskiyou County during the months of April and May. Four sampling sites will be selected in relatively high-population areas or in areas frequented by people. At each site, 24 discrete 24-hour samples will be taken during the sampling period. Background samples will be collected in an area distant to ethoprop applications. Replicate (collocated) samples will be collected for six dates (each Wednesday) at each sampling location.

Four sampling sites plus an urban background site will be selected by ARB personnel from the areas of Siskiyou County where potato farming is predominant. Sites will be selected for their proximity to the potato fields with considerations for both accessibility and security of the sampling equipment. The sites are near areas of historical use of ethoprop.

The samples will be collected by ARB personnel over a six week period from (tentatively) April 20 - May 29, 1998. 24-hour samples will be taken Monday through Friday (4 samples/week) at a flow rate of 3 L/minute.

Application Monitoring

The use pattern for ethoprop suggests that application-site monitoring should be conducted during the months of April or May in Siskiyou County, and that the monitoring be associated with applications of ethoprop to potatoes. A three day monitoring period will be established with desired sampling times as follows: Application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples, and two 24-hour samples. A minimum of four samplers will be positioned, one on each side of the field. A fifth sampler will be collocated at one position. Since ethoprop is extensively used in the area, background (before application) samples should be collected for a minimum of 12 hours at 3 liters/min. Ideally, samplers should be placed at a minimum of 20 meters from the field. If possible the samplers will be spaced equidistant from the edges of the field.

We will also provide in the monitoring report: 1) An accurate record of the positions of the monitoring equipment with respect to the field, 2) an accurate drawing of the monitoring site

showing the precise location of the meteorological equipment, trees, buildings, etc., 3) meteorological data collected at a minimum of 15 minute intervals including wind speed and direction, humidity, and comments regarding degree of cloud cover, 4) the elevation of each sampling station with respect to the field and 5) the orientation of the field with respect to North (identified as either true or magnetic north). Samples collected during fog episodes will be designated as such.

IV. Analysis

The method development results and "Standard Operating Procedures for the Analysis of Ethoprop in Ambient Air" (SOP) are included as Attachment I. The procedures consist of extraction of the sorbent with 2.5 mL of ethyl acetate followed by GC/MSD analysis. The method detection limit (MDL) and estimated quantitation limit (EQL) are approximately 1.05 ng per sample and 5.25 ng per sample respectively. The MDL calculation is: $MDL=3.14(S)$ for $n=7$, and the EQL is: $EQL=5 \times MDL$. The above MDL and EQL are estimates based on results presented in the attached SOP. The collection efficiency (recovery) of ethoprop at levels approaching the EQL, after exposure of spiked cartridges to field conditions, may be approximately 50% or less. The collection and recovery results presented in the SOP were based on spikes of 62.5 ng of ethoprop per cartridge, or about 10 times higher than the EQL. The average recovery of ethoprop at the 62.5 ng level was 62.3%.

VI. Quality Assurance

Field Quality Control for the ambient monitoring will include:

- 1) Five field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 3 L/minute (i.e., collocated with a background sample).
- 2) Five trip spikes prepared at the same level as the field spikes.
- 3) Five lab spikes prepared at the same level as the field and trip spikes.
- 4) Replicate samples will be taken for six dates at each sampling location.
- 5) A Trip blank will be obtained each week of sampling.

Field Quality Control for the application monitoring will include:

- 1) Four field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling). The field spikes will be obtained by sampling ambient air during background monitoring at the application site for the same duration as the background samples at 3 L/minute (i.e., collocated with background samples).
- 2) Four trip spikes prepared at the same level as the field spikes.

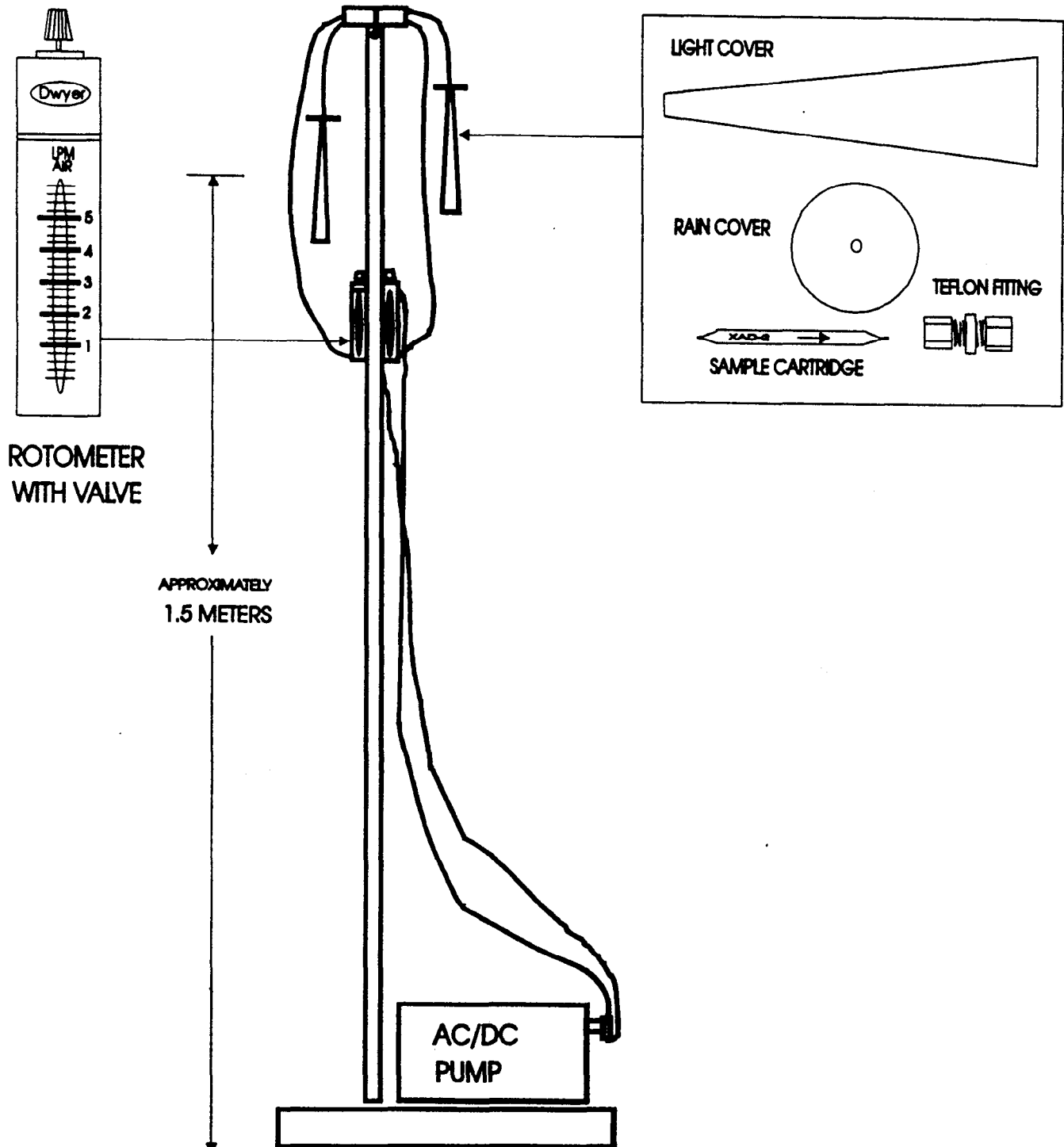
- 3) Four lab spikes prepared at the same level as the field and trip spikes.
- 4) Replicate samples will be taken for all samples at one of the sampling locations.
- 5) A Trip blank will be obtained.

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Rotameters will be calibrated prior to and after sampling in the field.

VII. Personnel

ARB personnel will consist of Kevin Mongar (Project Engineer) and Instrument Technicians from the Testing Section of ARB.

FIGURE 1. SAMPLE TREE



Attachment I

**Standard Operating Procedures for the
Analysis of Ethoprop in Ambient Air**

State of California
Air Resources Board
Monitoring and Laboratory Division/ELB

Draft Standard Operating Procedure for the Sampling and Analysis
of Ethoprop in Ambient Air
4/15/98 Version

Analyst: Ken Kiefer and R. Okamoto

Reviewed by: R. Okamoto
Kevin Mongar

1. SCOPE

This is a sorbent tube, solvent extraction, gas chromatography/mass spectrometry method for the determination of ethoprop from ambient air samples.

2. SUMMARY OF METHOD

The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest on dry ice or freezer until desorbed during sonication into 2.5 ml of ethyl acetate. The sorbent is spiked with 500ng of Diazinon-D₁₀ prior to extraction. The splitless injection volume is 4 ul. A gas chromatograph with a DB-17 capillary column and a quadrapole mass spectrometer (MS) is used for analysis. The MS detector is operated in selected ion monitoring mode.

3. INTERFERENCES/LIMITATIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. Co-eluting compounds trapped during sample collection may also interfere. A method blank must be analyzed with each batch of samples to detect any possible method interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Hewlett Packard 5890 chromatograph
Hewlett Packard 5971A mass selective detector
Hewlett Packard 8200 autosampler

Detector: 280°C
Injector: 250°C
Injector Liner: Double goose neck liner with glass wool
Column: J&W Scientific DB-17MS, 30 meter, 0.25 mm i.d., 0.25 um film thickness.

Pre-column: J&W Scientific deactivated fused silica, 2 meter, 0.25 mm i.d.

GC Temp. Program: Initial 50°C, hold 5 min., to 220°C @ 25°C/min., hold 2 min., to 280°C @ 5°C/min., hold 1 min.

Injector:

Pressure Pulse: Initial 6.4 psi, to 40 psi @ 99 psi/min, hold 1.31 min, to 6.4 psi @ 99 psi/min

Splitless: Purge on 2 min.

Gas Flows:

Column: Linear velocity: 32 cm/sec, electronic pressure control (6.4 psi @ 50 °C).

Auto Sampler:

Sample washes - 1, Sample pumps - 4, Sample Volume - 4 stops, Viscosity delay - Zero sec, Solvent A washes - 4, Solvent B washes - 4

Mass Spectrometer:

Electron Ionization

Selective Ion Monitoring; Ethoprop -158 (quant. ion, 100%), 97 (qual. ion, 25%), 126 (qual. ion, 30%), 139 (qual. Ion, 35%). Diazinon-D₁₀ - 183 (quant. ion, 100%), 99 (qual. ion, 27%), 304 (qual. Ion, 2%)

Tuning: PFTBA

B. AUXILIARY APPARATUS:

1. Glass amber vials, 8 mL capacity.
2. Glass amber vials, 4 mL capacity.
3. Vial Shaker, SKC, or equiv.
4. Sonicator, Branson 2210
5. Autosampler vials with septum caps.

C. REAGENTS

1. Ethyl Acetate, Pesticide Grade, or better
2. Ethoprop, 99 -% pure or better (e.g., from Chem Service).
3. Diazinon-D₁₀ 99, -% pure or better (e.g., from Cambridge Isotope Laboratories)

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses - 69, 219, 502. The criteria for the peak widths at $\frac{1}{2}$ the peak height is $0.5 \pm .05$. The criteria for relative abundances are; 69 - 100%; 219 - 60-70%; and 502 - 2-5%.
2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which results in possible carry-over contamination.
3. A 5 point calibration curve shall be analyzed with each batch of samples. A single point calibration check at the midpoint of the calibration curve may be substituted for the 5 point calibration curve provided that it is within 20% of the average response factor from an initial 5 point multipoint calibration curve and the calibration updated. Then a second midpoint calibration standard is run. If both midpoint calibrations are within 20% of each other then analysis of batch samples can proceed.
4. With each batch of samples a laboratory blank and two laboratory check samples will be run. A laboratory blank is a blank resin cartridge prepared and analyzed the same way the samples are analyzed. A laboratory check sample is a resin cartridge spiked with a known amount of standard. The check sample is prepped and analyzed the same way as the samples. Laboratory check samples need to be within 20% ($100 \times \text{difference/average}$) of each other and have recoveries that are $\pm 30\%$ of the theoretical spiked value.
5. At least one calibration check sample must be analyzed for each batch of ten samples. The response of the standard must be within 20% of the initial calibration analyses for the batch. If the calibration check is outside the limit then those samples in the batch after the last calibration check that was within the 20% limit need to be reanalyzed.
6. Carefully score the secondary section end of the sampled XAD-2 tube above the glasswool and break at the score. Remove the glass wool plug from the secondary end of the XAD-2 tube with forceps and place it into a 4 mL amber colored sample vial. Pour the backup portion of the XAD-2 into the same vial.
7. Pour the primary XAD into a 8 ml vial. Remove the glasswool plug and put it into the 8 ml vial. Rinse the tube with 2.5 ml of ethyl acetate and pour rinse into the 8 ml vial.
8. Place the sample vial on a desorption shaker (or ultra sonic water-bath) for 30 minutes. Remove the ethoprop extract and store in a second vial at -20°C until analysis.
9. Add a 270 ul aliquot of the sample extract to the autosampler vial. Spike the sample extract with 30ul of 1000 pg/ul diazinon- D_{10} .

10. After calibration of the GC system, inject 4.0 ul of the extract. If the resultant peaks for ethoprop has a measured concentration greater than that of the highest standard injected, dilute the sample and re-inject.
11. Calculate the concentration in ng/mL based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.
12. The atmospheric concentration is calculated according to:

$$\text{Conc., ng/m}^3 = (\text{Extract Conc., ng/mL} \times 2.5 \text{ mL}) / \text{Air Volume Sampled, m}^3$$

6. QUALITY ASSURANCE

A. INSTRUMENT REPRODUCIBILITY

Five injections of 4 ul each were made of Ethoprop standards at three concentrations in order to establish the reproducibility of this instrument. This data (Testing Section lab, 12/11/97) is shown in Table 1.

TABLE 1. Instrument Reproducibility

Diazinon-D ₁₀ Conc. (ng/ml)	Diazinon-D ₁₀ Response	Ethoprop Conc. (ng/ml)	Ethoprop Response	Amt. Ratio	Resp Ratio	Response Ratio RSD
100	2743	12.5	582	.125	.212	5.92
100	2544	12.5	581	.125	.228	
100	2757	12.5	624	.125	.226	
100	2691	12.5	673	.125	.250	
100	2544	12.5	581	.125	.228	
100	2628	50	2564	.50	.976	3.84
100	2454	50	2533	.50	1.03	
100	2491	50	2573	.50	1.03	
100	2467	50	2601	.50	1.05	
100	2165	50	2347	.50	1.08	
100	2972	250	16325	2.5	5.49	3.06
100	2781	250	16322	2.5	5.87	
100	2650	250	15798	2.5	5.96	
100	2089	250	12040	2.5	5.76	
100	2877	250	16498	2.5	5.73	

B. CALIBRATION

Initial Calibration

A five point calibration curve was made on 12/11/97. The calibration range was 250 ng/mL to 12.5 ng/mL Ethoprop. The corresponding response factor regression equation is:

$$\text{Response Ratio} = (2.2) * (\text{Amount Ratio}) \text{ RF Rel. Std. Dev. } = 7.2\%$$

where:

Response Ratio = (Ethoprop response)/(Diazinon-D₁₀ response)

Amount Ratio = (Ethoprop concentration)/Diazinon-D₁₀ concentration)

Using EPA format, to minimize the number of calibrations performed, a midpoint (single point) calibration is performed daily. A laboratory check sample is run daily. If the two analysis are within 20% of the assigned value, then analysis will begin. After every ten samples a calibration sample will be analyzed to verify the system is still in calibration. Alternately a full multi-point calibration curve can be performed before analyzing a batch of samples.

Linearity

A linear regression was also performed on the calibration curve made on 12/11/97.

Resp Ratio = (2.18)*(amount ratio) - 6.65e⁻²

R² = .999

C. MINIMUM DETECTION LIMIT

Detection limit is based on USEPA detection limit calculation. Using the analysis of seven replicates of a low level matrix spikes, the method detection limit (MDL), and the estimated quantitation limit (EQL) for ethoprop were calculated by:

$$MDL = 3.14 * s$$

$$EQL = 5 * MDL$$

where:

s = the standard deviation of the concentration of the concentration calculated for the seven replicate spikes.

Given s = 1.07 for the seven samples, the MDL and EQL are calculated as follows, MDL and PQL values are rounded to one place.

$$MDL = 3.14 * 1.07 = 3.36 \text{ pg/ul}$$

$$EQL = 5 * 3.36 = 16.8 \text{ pg/ul}$$

Based on the 2.5 mL extraction volume and assuming a sample volume of 4.32 m³ (3 lpm for 24 hours) the ambient concentration of ethoprop at the EQL is :

$$(16.8 \text{ ng/mL})(2.5 \text{ mL}) / (4.32 \text{ m}^3) = 9.72 \text{ ng/m}^3 \text{ per 24-hour sample}$$

The MDL and EQL can be lowered by approximately eight fold by using lower concentration standards to spike the resin and by increasing the MS electron multiplier voltage. Prior to doing ethoprop analysis the MDL and EQL will be recalculated using lower concentration standards and a higher electron multiplier voltage.

D. COLLECTION AND EXTRACTION EFFICIENCY (RECOVERY)

62.5 ng of ethoprop standard were spiked on the primary section of each of six XAD-2 sampling tubes. The spiked tubes were then subjected to an air flow of 3 lpm for 24 hours. The samplers were set-up at 13th and T St. in Sacramento at an ambient temperature of approximately 30°C (maximum). The primary sections were then extracted with ethyl acetate and analyzed. Percent recoveries of ethoprop from primary sections of three tubes analyzed within one week of sampling were 64.8%, 61.7%, 62.3% with an average of 62.9% and the percent recoveries of three tubes analyzed within two weeks of sampling were 56.6%, 60.9%, and 67.8 with an average of 61.7%. Percent recovery of ethoprop at levels approaching the EQL, after exposure of spiked cartridges to field conditions, may be 50% or less.

E. STORAGE STABILITY

Storage stability studies were conducted over a 4 week period. The primary sections of 19 tubes were spiked with 62.5 ng of Ethoprop. The spiked tubes were stored in the freezer at -20°C and extracted/analyzed on storage weeks 1,2,3 and 4. Four tubes were analyzed on week 1 and 5 tubes each were analyzed on weeks 2, 3, and 4. The storage recoveries (average results) were 79.1%, 81.9%, 64.7% and 77.3% for weeks 1,2,3 and 4 respectively.

A second set of fifteen tubes were spiked with 1250 ngs of Ethoprop. The spiked tubes were stored in the freezer at -20°C and extracted/analyzed on storage weeks 1, 3 and 4. Five tubes each were analyzed on week 1, 3, and 4. The storage recoveries (average results) were 97.8%, 75.2%, and 91.9% respectively.

F. BREAKTHROUGH

The primary sections of four tubes were spiked with 750 ng ethoprop/tube then run for 24 hours at 3 lpm (see Section D above). No ethoprop was detected in the back-up resin bed of any of the tubes.

G. Safety

Ethoprop is highly toxic if inhaled, moderately toxic if ingested, and slightly toxic via dermal exposure. The LD₅₀ ranges is 16.7 mg/kg/day for rats. The 4-hour inhalation LC50 in rats is .136 mg/L for male rats and .002 mg/L for female rats. The TWA is .1 mg/m³.

APPENDIX II

LABORATORY REPORT



er M. Rooney
Secretary for
Environmental
Protection

Air Resources Board

Barbara Riordan, Chairman
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Pete Wilson
Governor

TO: Cindy Castronovo
Manager, Testing Section

FROM: Robert Okamoto *Rad*
Lead Laboratory Chemist, Testing Section

DATE: December 15, 1998

SUBJECT: ETHOPROP LABORATORY RESULTS AND METHOD DEVELOPMENT

Included in the attached report are the following items.

1. Ambient and application ethoprop analytical results.
2. Ethoprop standard operating procedure.
3. Quality assurance report.
4. Spike and blank results.
5. Background blank levels
 - a. Chromatograms and extracted ion profiles.
 - b. An ethoprop field spike total ion chromatogram.
 - c. Extracted ion profile for ethoprop in a sample.
 - d. Extracted ion profile for ethoprop at the estimated quantitation limit.
 - e. Extracted ion profile for ethoprop in the resin blank.

State of California
California Environmental Protection Agency
Air Resources Board

Testing Section Laboratory Report

Ethoprop Method Development and Ethoprop Analytical Results for Ambient
Monitoring Samples

Engineering and Laboratory Branch
Monitoring and Laboratory Division

Project No. C98-005 and C98-006
Sept. 28, 1998

1.0 Introduction

The Air Resources Board (ARB) staff developed an air sampling and analysis method for ethoprop. Ambient air samples were collected and analyzed by ARB staff. This report covers ethoprop method development, ethoprop analytical results, and quality assurance results.

2.0 Method Development and Standard Operating Procedure.

In the fall of 1997 an isotope dilution ethoprop procedure was developed and validated. The standard operating procedure (SOP) also includes procedures that more closely match US Environmental Protection Agency methodology. The standard operating procedure is given in Attachment 1.

3.0 Ambient Sample Results.

3.1 Samples Received:

Ambient Samples

148 ambient samples
5 field spikes
5 trip spikes
5 laboratory spikes
6 trip blanks

<u>Date Samples Received</u>	<u>Date Analysis Completed</u>
5/04/98	5/07/98
5/11/98	5/20/98
5/18/98	6/06/98
5/28/98	6/09/98
6/07/98	6/17/98

Presented in Table 1 are the results of the analysis of the ethoprop ambient samples. Also included in Table 1 are the dates the laboratory received and analyzed the samples. An asterisk to the right of the ethoprop amount denotes the sample was analyzed in duplicate and the results are the average of the two analyses.

Table 1. Ethoprop Ambient Results

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
1	MAC01	05/04/98	05/07/98	5.89E+0
2	DOR01	05/04/98	05/07/98	<MDL
3	TLB01	05/04/98	05/07/98	<MDL
4	NEW01	05/04/98	05/07/98	<MDL
5	LAV01	05/04/98	05/07/98	<MDL
6	LAV01D	05/04/98	05/07/98	<MDL
7	MAC02	05/04/98	05/07/98	<MDL
8	DOR02	05/04/98	05/07/98	<MDL
9	TLB02	05/04/98	05/07/98	<MDL
10	NEW02	05/04/98	05/07/98	<MDL*
11	LAV02	05/04/98	05/07/98	<MDL
12	LAV02D	05/04/98	05/07/98	<MDL
13	MAC03	05/04/98	05/07/98	<MDL
14	DOR03	05/04/98	05/07/98	<MDL
15	TLB03	05/04/98	05/07/98	<MDL
16	NEW03	05/04/98	05/07/98	<MDL
17	LAV03	05/04/98	05/07/98	<MDL
18	LAV03D	05/04/98	05/07/98	<MDL
19	TB03	05/11/98	05/20/98	<MDL
20	LAV04	05/11/98	05/18/98	<MDL
21	FS1	05/11/98	05/20/98	1.13E+1
22	FS2	05/11/98	05/20/98	1.19E+1
23	NEW04	05/11/98	05/18/98	<MDL
24	TLB04	05/11/98	05/18/98	<MDL
25	DOR04	05/11/98	05/18/98	<MDL
26	MAC04	05/11/98	05/18/98	5.84E+0
27	LAV05	05/11/98	05/18/98	<MDL
28	FS3	05/11/98	05/20/98	1.23E+1
29	FS4	05/11/98	05/20/98	1.36E+1
30	FS5	05/11/98	05/20/98	1.23E+1
31	NEW05	05/11/98	05/18/98	<MDL
32	TLV05	05/11/98	05/18/98	Det
33	DOR05	05/11/98	05/18/98	<MDL
34	MAC05	05/11/98	05/18/98	<MDL

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
34	MAC05	05/11/98	05/18/98	< MDL
35	LAV06	05/11/98	05/18/98	< MDL
36	LAV06D	05/11/98	05/18/98	Det
37	NEW06	05/11/98	05/18/98	< MDL
38	NEW06D	05/11/98	05/18/98	< MDL
39	TLB06	05/11/98	05/18/98	Det
40	TLB06D	05/11/98	05/18/98	< MDL
41	DOR06	05/11/98	05/18/98	< MDL
42	DOR06D	05/11/98	05/18/98	< MDL
43	MAC06	05/11/98	05/18/98	< MDL
44	MAC06D	05/11/98	05/19/98	< MDL*
45	LAV07	05/11/98	05/19/98	Det
46	NEW07	05/11/98	05/19/98	Det
47	TLB07	05/11/98	05/19/98	Det
48	DOR07	05/11/98	05/19/98	< MDL
49	MAC07	05/11/98	05/19/98	< MDL
50	TB07			NA ¹
51	TS1	05/11/98	05/20/98	1.22E+1
52	TS2	05/11/98	05/20/98	1.12E+1
53	TS3	05/11/98	05/20/98	1.07E+1
54	TS4	05/11/98	05/20/98	1.32E+1 ²
55	TS5	05/11/98	05/20/98	1.17E+1
56	LAV08	05/18/98	06/05/98	Det
57	NEW08	05/18/98	06/05/98	< MDL
58	TLB08	05/18/98	06/05/98	Det
59	DOR08	05/18/98	06/05/98	Det
60	MAC08	05/18/98	06/05/98	< MDL
61	LAV09	05/18/98	06/05/98	< MDL
62	NEW09	05/18/98	06/05/98	< MDL
63	TLV09	05/18/98	06/05/98	< MDL
64	DOR09	05/18/98	06/05/98	< MDL
65	MAC09	05/18/98	06/05/98	< MDL*
66	LAV10	05/18/98	06/05/98	< MDL
67	LAV10D	05/18/98	06/05/98	< MDL
68	NEW10	05/18/98	06/05/98	< MDL

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
69	NEW10D	05/18/98	06/05/98	< MDL
70	TLB10	05/18/98	06/05/98	Det
71	TLB10D	05/18/98	06/05/98	Det
72	DOR10	05/18/98	06/05/98	< MDL
73	DOR10D	05/18/98	06/05/98	< MDL
74	MAC10	05/18/98	06/05/98	< MDL
75	MAC10D	05/18/98	06/05/98	< MDL*
76	LAV11	05/18/98	06/05/98	< MDL
77	NEW11	05/18/98	06/06/98	< MDL
78	TLB11	05/18/98	06/06/98	< MDL
79	DOR11	05/18/98	06/06/98	1.19E+1
80	MAC11	05/18/98	06/06/98	< MDL
81	TB11	05/18/98	06/06/98	< MDL
82	MAC12	05/28/98	06/08/98	< MDL
83	DOR12	05/28/98	06/08/98	< MDL
84	LAV12	05/28/98	06/08/98	< MDL
85	NEW12	05/28/98	06/08/98	< MDL
86	TLB12	05/28/98	06/08/98	< MDL
87	LAV13	05/28/98	06/08/98	< MDL
88	NEW13	05/28/98	06/08/98	< MDL
89	TLV13	05/28/98	06/08/98	< MDL
90	DOR13	05/28/98	06/08/98	< MDL
91	MAC13	05/28/98	06/08/98	Det* ¹
92	LAV14	05/28/98	06/08/98	< MDL
93	LAV14D	05/28/98	06/09/98	< MDL
94	NEW14	05/28/98	06/09/98	Det
95	NEW14D	05/28/98	06/09/98	Det
96	TLB14	05/28/98	06/09/98	Det
97	TLB14D	05/28/98	06/09/98	Det
98	DOR14	05/28/98	06/09/98	< MDL
99	DOR14D	05/28/98	06/09/98	< MDL
100	MAC14	05/28/98	06/09/98	< MDL
101	MAC14D	05/28/98	06/09/98	< MDL
102	LAV15	05/28/98	06/09/98	< MDL
103	NEW15	05/28/98	06/09/98	< MDL

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
104	TLB15	05/28/98	06/09/98	Det
105	DOR15	05/28/98	06/09/98	< MDL
106	MAC15	05/28/98	06/09/98	< MDL
107	TB15	05/28/98	06/09/98	< MDL
108	LAV16	06/07/98	06/16/98	< MDL
109	NEW16	06/07/98	06/16/98	< MDL
110	TLB16	06/07/98	06/16/98	< MDL
111	DOR16	06/07/98	06/16/98	< MDL
112	MAC16	06/07/98	06/16/98	< MDL
113	LAV17	06/07/98	06/16/98	< MDL*
114	NEW17	06/07/98	06/16/98	< MDL
115	TLB17	06/07/98	06/16/98	< MDL
116	DOR17	06/07/98	06/16/98	< MDL
117	MAC17	06/07/98	06/16/98	< MDL
118	LAV18	06/07/98	06/16/98	< MDL
119	LAV18D	06/07/98	06/17/98	< MDL*
120	NEW18	06/07/98	06/16/98	< MDL
121	NEW18D	06/07/98	06/16/98	< MDL
122	TLB18	06/07/98	06/16/98	< MDL
123	TLB18D	06/07/98	06/16/98	< MDL
124	DOR18	06/07/98	06/16/98	< MDL
125	DOR18D	06/07/98	06/16/98	< MDL
126	MAC18	06/07/98	06/16/98	< MDL
127	MAC18D	06/07/98	06/16/98	< MDL
128	LAV19	06/07/98	06/16/98	< MDL
129	NEW19	06/07/98	06/16/98	< MDL
130	TLB19	06/07/98	06/16/98	< MDL
131	DOR19	06/07/98	06/16/98	< MDL
132	MAC19	06/07/98	06/16/98	8.36E+0
133	LAV20	06/07/98	06/16/98	< MDL*
134	NEW20	06/07/98	06/16/98	< MDL
135	TLB20	06/07/98	06/16/98	< MDL
136	DOR20	06/07/98	06/16/98	< MDL
137	MAC20	06/07/98	06/16/98	7.88E+0

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
138	LAV21	06/07/98	06/17/98	<MDL
139	NEW21	06/07/98	06/17/98	<MDL
140	TLB21	06/07/98	06/17/98	<MDL
141	DOR21	06/07/98	06/17/98	<MDL
142	MAC21	06/07/98	06/17/98	<MDL
143	LAV22	06/07/98	06/17/98	<MDL*
144	LAV22D	06/07/98	06/17/98	<MDL
145	NEW22	06/07/98	06/17/98	<MDL
146	NEW22D	06/07/98	06/17/98	<MDL
147	TLB22	06/07/98	06/17/98	<MDL
148	TLB22D	06/07/98	06/17/98	<MDL
149	DOR22	06/07/98	06/17/98	<MDL
150	DOR22D	06/07/98	06/17/98	<MDL
151	MAC22	06/07/98	06/17/98	<MDL
152	MAC22D	06/07/98	06/17/98	<MDL
153	TB22	06/07/98	06/17/98	<MDL
154	LAV23	06/07/98	06/17/98	<MDL
155	NEW23	06/07/98	06/17/98	<MDL
156	TLB23	06/07/98	06/17/98	Det
157	DOR23	06/07/98	06/17/98	<MDL
158	MAC23	06/07/98	06/17/98	Det
159	LAV24	06/07/98	06/17/98	<MDL
160	NEW24	06/07/98	06/17/98	<MDL
161	TLB24	06/07/98	06/17/98	<MDL
162	DOR24	06/07/98	06/17/98	<MDL
163	MAC24	06/07/98	06/17/98	<MDL
164	TB24	06/07/98	06/17/98	<MDL
	LS1	05/11/98	05/20/98	9.97E+0
	LS2	05/11/98	05/20/98	1.10E+1
	LS3	05/11/98	05/20/98	1.09E+1
	LS4	05/11/98	05/20/98	1.01E+1
	LS5	05/11/98	05/20/98	1.11E+1

¹NA = not analyzed, sample loss

²One sample was above and the other sample was below the MDL

* Average of duplicate analysis

MDL = .947 ng/sample

Det = <EQL of 4.73 ng/sample but \geq MDL

4.0 Ethoprop Ambient Analytical Quality Control

With the analysis of each batch of samples a series of calibration samples and QA samples were run. A summary of the results is given in this section.

4.1 Mass spectrometer tune

Prior to the analysis of a batch of samples the mass spectrometer was manually tuned. Tune parameters are given in the ethoprop SOP (section 5.1).

4.2 Laboratory solvent blanks

Prior to the analysis of a sample analysis run a laboratory solvent blank was analyzed. Given in Table 2 are the results of the laboratory solvent blanks for the seven sample batches. No ethoprop was detected in any of the laboratory solvent blanks.

Table 2. Laboratory solvent blanks

Sample Name	Date	Ethoprop Amount (ng/sample)
B985061	5/06/98	<MDL*
B985156	5/18/98	<MDL
B986041	6/04/98	<MDL
B9860741	6/08/98	<MDL
B9861541	6/15/98	<MDL
B9861541	6/15/98	<MDL
B9861742	6/17/98	<MDL

*BKG = Amount at background level.

4.3 Calibration.

A 5-point multi-point calibration was run prior to each batch of samples.

4.4 Laboratory control spikes

Prior to the analysis of each batch of samples, two laboratory control spikes (LCS) were run. A sample batch is defined as all the samples that are prepped during the same period of time. A LCS is a resin cartridge spiked with 10 ngs or 20 ngs of ethoprop. The check sample is prepared and analyzed the same way as the samples. LCS recoveries ranged from 78%-120% and the relative difference between samples in each set ranged from 3.72% - 28.3%. The results are presented in Table 3.

Table 3. Laboratory control spike results.

Sample Name	Date Analyzed	Ethoprop Amount (ng/sample)	Ethoprop Expected (ng/sample)	Percent Recovery	Relative difference
LC29	5/07/98	7.8	10	78%	
LC30	5/07/98	10.3	10	103%	28.3%
LC31	5/18/98	21.6	20	108%	
LC32	5/18/98	20.9	20	104%	3.72%
LC34	6/05/98	17.0	20	85%	
LC35	6/05/98	18.1	20	91%	6.54%
LC38	6/08/98	23.9	20	120%	
LC39	6/08/98	22.2	20	111%	7.51%
LC40	6/16/98	20.9	20	105%	
LC41	6/16/98	21.9	20	110%	4.64%

Relative difference = $100 * (\text{sample1} - \text{sample2}) / \text{average}$

4.5 Laboratory control blanks

A single laboratory control blank (LCB) is run prior to the analysis of each sample batch. The LCB blank sample cartridge is prepared and analyzed the same way the samples are analyzed. The LCB results are presented in Table 4. <MDL means the level in the blanks were lower than the detection level.

Table 4. Laboratory control blank results

Sample Name	Date Analyzed	Ethoprop Amount (ng/sample)
LB13	5/07/98	<MDL*
LB15	5/18/98	<MDL
LB16	6/05/98	<MDL
LB18	6/08/98	<MDL
LB19	6/16/98	<MDL

* <MDL = Amount below the method detection limit

4.6 Calibration check samples

Calibration check samples (CCS) are analyzed with each set of samples analyzed. A CCS is run after every tenth sample in each analytical set. CCS samples are run to ensure instrument drift does not exceed 20%. CCS sample results are given in Table 5. The average CCS percent recovery was 94.8% of the expected ethoprop amount with a relative standard deviation of 11.4%

Table 5. Calibration check sample results

Sample Name	Date Run	Ethoprop Amount (ng/sample)	Ethoprop Expected (ng/sample)	Percent Recovery
CC850601	5/07/98	23.9	20	120%
CC850602	5/07/98	22.6	20	113%
CC851501	5/18/98	17.9	20	90%
CC851502	5/18/98	19.9	20	100%
CC850603	5/19/98	19.7	20	98%
CC850604	5/19/98	16.4	20	82%
CC850605	5/19/98	17.4	20	87%
CC860401	6/05/98	16.5	20	83%
CC860402	6/05/98	16.9	20	85%
CC860403	6/05/98	16.8	20	84%
CC860404	6/06/98	16.5	20	82%
CC860405	6/06/98	18.9	20	94%
CC860405	6/09/98	21.1	20	105%
CC860406	6/09/98	20.1	20	101%
CC861501	6/16/98	18.1	20	90%
CC861503	6/16/98	21.1	20	106%
CC861505	6/16/98	18.4	20	92%
CC861701	6/17/98	16.9	20	84%
CC861702	6/17/98	20.7	20	103%
CC861703	6/17/98	19.8	20	99%

4.7 Duplicate analysis

Duplicate analysis is performed on every tenth sample in a each set of samples analyzed. Results are given in Table 6. Relative difference was calculated on duplicate pairs when the values were at or higher than the EQL. The relative difference was 3.80%.

Table 6. Duplicate analysis results

Sample Name	Ethoprop Amount (ng/sample)	Average (ng/sample)	Relative Difference ⁴
NEW02-1	<MDL ¹		
NEW02-2	<MDL	NQ ³	NC ⁵
MAC05-1	<MDL		
MAC05-2	<MDL	NQ	NC
MAC06D-1	<MDL		
MAC06D-2	<MDL	NQ	NC
TS4-1	1.29E + 1		
TS4-2	1.34E + 1	1.32E + 1	3.80%
MAC09-1	<MDL		
MAC09-2	<MDL	NQ	NC
MAC10D-1	<MDL		
MAC10D-2	<MDL	NQ	NC
MAC13-1	<MDL		
MAC13-2	DET ²	NQ	NC
MAC14D-1	<MDL		
MAC14D-2	<MDL	NQ	NC
CHW22-1	<MDL		
CHW22-2	<MDL	NQ	NC
LAV18D-1	<MDL		
LAV18D-2	<MDL	NQ	NC
LAV20-1	<MDL		
LAV20-2	<MDL	NQ	NC

¹ <MDL = level below the method detection level² Det = Level below the estimated quantitation limit but above the MDL³ NQ = not quantitated⁴ Rel Diff = $100 * (\text{Sample1} - \text{Sample2}) / \text{Ave}$ ⁵ NC = not calculated

5.0 Field, trip, and laboratory spikes and trip blanks

Five laboratory spikes, five trip spikes and five field spikes were analyzed for the ambient ethoprop test.

5.1 Laboratory spikes

Five laboratory spikes were spiked with 10 ngs of ethoprop on 5/01/98 and stored in the Testing's Laboratory freezer until they were analyzed on 5/20/98. The laboratory spike results are given in Table 7. The average percent recovery was 106% and the relative standard deviation was 5.22%.

Table 7. Laboratory spikes results

Sample Name	Date Spiked	Date Analyzed	Ethoprop Amount (ng/sample)	Amount Ethoprop Spiked (ng/sample)	Percent Recovery
LS01	5/01/98	5/20/98	9.97	10.0	99.7%
LS02	5/01/98	5/20/98	11.0	10.0	110%
LS03	5/01/98	5/20/98	10.9	10.0	109%
LS04	5/01/98	5/20/98	10.1	10.0	101%
LS05	5/01/98	5/20/98	11.1	10.0	111%

5.2 Trip spikes

A series of 5 trip spikes were spiked with 10.0 ngs of ethoprop on 5/01/98. Trip spikes were taken to the sampling site and returned to laboratory along with a batch of samples, which were analyzed on 5/20/98. The trip spike results are given in Table 8. The average recovery was 123% and the relative standard deviation was 6.87%.

Table 8. Trip spike results

Sample Name	Date Spiked	Date Analyzed	Ethoprop Amount (ng/sample)	Amount Ethoprop Spiked (ng/sample)	Percent Recovery
FS01	5/01/98	5/20/98	11.3	10	113%
FS02	5/01/98	5/20/98	11.9	10	119%
FS03	5/01/98	5/20/98	12.3	10	123%
FS04	5/01/98	5/20/98	13.6	10	136% *
FS05	5/01/98	5/20/98	12.3	10	123%

*Recovery exceeded 130%

5.3 Field spikes

A series of 5 field spikes were spiked with 10 ngs of Ethoprop on 5/01/98. Field spikes were taken to the sampling site and ambient air was sampled on the field spikes. An unspiked collocated sample was taken concurrently with the field spikes. The field spike was returned to the laboratory along with a batch of samples. The field spike results are given in Table 9. The average recovery of the field spikes was 118% with a relative standard deviation of 8.00%.

Table 9. Field spike results

Sample Name	Date Spiked	Date Analyzed	Ethoprop Amount (ng/sample)	Amount Ethoprop Spiked (ng/sample)	Percent Recovery
TS01	5/01/98	5/20/98	12.2	10.0	122%
TS02	5/01/98	5/20/98	11.2	10.0	112%
TS03	5/01/98	5/20/98	10.7	10.0	107%
TS04	5/01/98	5/20/98	13.2	10.0	132% *
TS05	5/01/98	5/20/98	11.7	10.0	117%

*Recovery exceeded 130%.

5.4 Trip blanks

Four trip blanks were taken to the sampling site and returned to the laboratory with a batch of samples. The trip blank result is given in Table 10.

Table 10. Trip blank results

Sample Name	Date Analyzed	Amount in Sample (ng/sample)
TB03	5/19/98	<MDL*
TB07	NA	NA
TB11	6/06/98	<MDL
TB15	6/09/98	<MDL
TB22	6/18/98	<MDL
TB24	6/18/98	<MDL

* <MDL = less than the method detection limit

NA = Sample not analyzed due to loss of sample.

6.0 Application Sample Results.

6.1 Samples Received:

Application Samples

35 application samples

3 field spikes

3 trip spikes

4 laboratory spikes

1 trip blank

<u>Date Samples Received</u>	<u>Date Analysis Completed</u>
5/19/98	7/13/98

All samples were initially analyzed on 5/20/98. Samples exceeding the highest standard level were reanalyzed on July 13, 1998 along with the laboratory control spikes and blank that were extracted with this batch of samples. The control spikes and blank that were initially analyzed on 5/20/98 were reanalyzed on 7/13/98. The control samples were still within performance parameters and thus the samples that were extracted at the same time as the laboratory controls were still considered valid and analyzed.

Presented in Table 11 are the results of the analysis of the ethoprop application samples. Also included in Table 11 are the dates the laboratory received and analyzed the samples.

Table 11. Ethoprop Application Results

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
1	WB	05/19/98	05/20/98	Det
2	WFS1	05/19/98	05/20/98	4.65E + 1
3	SB	05/19/98	05/20/98	< MDL
4	SFS2	05/19/98	05/20/98	4.55E + 1
5	EB	05/19/98	05/20/98	< MDL
6	EFS3	05/19/98	05/20/98	5.19E + 1
7	NB	05/19/98	05/20/98	< MDL
8	E1	05/19/98	05/20/98	7.19E + 1
9	E1D	05/19/98	05/20/98	8.14E + 1

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
10	S1	05/19/98	05/20/98	5.56E + 1 *
11	W1	05/19/98	05/20/98	3.99E + 1
12	N1	05/19/98	05/20/98	8.39E + 1
13	E2	05/19/98	05/20/98	2.93E + 1
14	E2D	05/19/98	05/20/98	3.32E + 1
15	S2	05/19/98	05/20/98	2.76E + 1
16	W2	05/19/98	05/20/98	2.47E + 1
17	N2	05/19/98	05/20/98	1.08E + 1
18	E3	05/19/98	05/20/98	3.91E + 1
19	E3D	05/19/98	05/20/98	3.44E + 1
20	S3	05/19/98	05/20/98	1.41E + 2
21	W3	05/19/98	05/20/98	8.67E + 1 *
22	N3	05/19/98	05/20/98	6.93E + 1
23	E4	05/19/98	05/20/98	1.95E + 2
24	E4D	05/19/98	05/20/98	2.12E + 2
25	S4	05/19/98	05/20/98	1.28E + 2
26	W4	05/19/98	05/20/98	1.26E + 1
27	N4	05/19/98		NA ¹
28	E5	05/19/98	07/14/98	4.27E + 2
28	E5BKP	05/19/98	07/14/98	5.71E + 0
29	E5D	05/19/98	07/14/98	4.85E + 2
29	E5DBKP	05/19/98	07/14/98	<MDL
30	S5	05/19/98	07/14/98	2.13E + 2
30	S5BKP	05/19/98	07/14/98	<MDL
31	W5	05/19/98	05/20/98	8.26E + 1
32	N5	05/19/98	07/14/98	8.29E + 1
32	N5BKP	05/19/98	07/14/98	<MDL
33	E6	05/19/98	07/14/98	3.17E + 2
33	E6BKP	05/19/98	07/14/98	<MDL
34	E6D	05/19/98	07/14/98	3.17E + 2
34	E6DBKP	05/19/98	07/14/98	<MDL
35	S6	05/19/98	07/14/98	8.34E + 2
36	W6	05/19/98	05/20/98	2.76E + 1
37	N6	05/19/98	05/20/98	9.72E + 1
38	TB	05/19/98	05/20/98	<MDL

Log ID	Sample Name	Date Received	Date Analyzed	Ethoprop Amount (ng/sample)
39	TS1	05/19/98	05/20/98	4.86E + 1
40	TS2	05/19/98	05/20/98	4.81E + 1 *
41	TS3	05/19/98	07/14/98	5.16E + 1
	LS1	05/19/98	07/14/98	4.53E + 1 *
	LS2	05/19/98	07/14/98	4.75E + 1
	LS3	05/19/98	07/14/98	4.52E + 1
	LS4	05/19/98	07/14/98	4.10E + 1

¹NA = sample not analyzed

*Results average of two analyses

7.0 Ethoprop Ambient Analytical Quality Control

With the analysis of each batch of samples a series of calibration samples and QA samples were run. A summary of the results is given in this section.

7.1 Mass spectrometer tune

Prior to the analysis of a batch of samples the mass spectrometer was manually tuned. Tune parameters are given in the ethoprop SOP (section 5.1).

7.2 Laboratory solvent blanks

Prior to the analysis of a set of sample analyzed a laboratory solvent blank was analyzed. Three batches of application ethoprop samples were analyzed. Given in Table 12 are the results of the laboratory solvent blanks for the three sample batches. No ethoprop was detected in any of the laboratory solvent blanks

Table 12. Laboratory solvent blanks

Sample Name	Date	Ethoprop Amount (ng/sample)
B985191	5/19/98	<MDL*
B985201	5/20/98	<MDL
B987131	7/13/98	<MDL

*MDL = Amount below the method detection level.

7.3 Calibration.

A 5-point multi-point calibration was run prior to each batch of samples.

7.4 Laboratory control spikes

Prior to the analysis of each batch of samples, two laboratory control spikes (LCS) were run. A LCS is a resin cartridge spiked with 20 ngs of ethoprop. The check sample is prepared and analyzed the same way as the samples. LCS recoveries ranged from 90.7%-129% and the relative difference between samples in each set ranged from 15.2% - 23.1%. The results are presented in Table 13.

Table 13. Laboratory control spike results.

Sample Name	Date Analyzed	Ethoprop Amount (ng/sample)	Ethoprop Expected (ng/sample)	Percent Recovery	Relative difference
LC37	5/20/98	20.5	20	102%	
LC38	5/20/98	25.6	20	129%	23.1%
LC36	7/13/98	21.1	20	106%	
LC37	7/13/98	18.1	20	90.7%	15.2%

Rel diff = $100 * (\text{sample1} - \text{sample2}) / \text{average}$

7.5 Laboratory control blanks

A single laboratory control blank (LCB) is run prior to the analysis of each sample batch. The LCB blank sample cartridge is prepared and analyzed the same way the samples are analyzed. Blank, LB17, was reanalyzed with the reanalysis of ethoprop samples initially analyzed on 5/20/98. The LCB results are presented in Table 14. <MDL means the level in the blanks were lower than the detection level.

Table 14. Laboratory control blank results

Sample Name	Date Analyzed	Ethoprop Amount (ng/sample)
LB17	5/21/98	<MDL
LB17	7/13/98	<MDL

* <MDL = Amount below the method detection limit

7.6 Calibration check samples

Calibration check samples (CCS) are analyzed with each set of samples analyzed. A CCS is run after every tenth sample in a sample batch. CCS samples are run to ensure instrument drift does not exceed 20%. CCS sample results are given in Table 15. The average CCS percent recovery was 97.6% of the expected

ethoprop amount with a relative standard deviation of 9.9%

Table 15. Calibration check sample results

Sample Name	Date Run	Ethoprop Amount (ng/sample)	Ethoprop Expected (ng/sample)	Percent Recovery
CC852002	5/21/98	34.6	40	86%
CC852001	5/21/98	37.2	40	93%
CC852003	5/21/98	40.8	40	102%
CC852004	5/21/98	20.4	20	102%
CC850603	5/20/98	20.4	20	102%
CC850604	5/20/98	10.9	10	109%
CC851901	5/20/98	22.2	20	111%
CC861902	5/20/98	20.1	20	101%
CC871301	7/14/98	16.6	20	83%
CC852004	7/14/98	17.5	20	88%

7.7 Duplicate analysis

Duplicate analysis is performed on every tenth sample in a set of sample analyzed. Results are given in Table 16. Relative difference was calculated on duplicate pairs when the values were at or higher than the EQL. The relative difference ranged from 1.73%-19.68%.

Table 16. Duplicate analysis results

Sample Name	Ethoprop Amount (ng/sample)	Average (ng/sample)	Relative Difference
S1-1	5.47E + 1		
S1-2	5.65E + 1	5.56E + 1	3.34%
W3-1	8.68E + 1		
W3-2	8.66E + 1	8.67E + 1	1.73%
TS2-1	4.33E + 1		
TS2-2	5.28e + 1	4.81E + 1	19.68%
LS1-1	4.61E + 1		
LS1-2	4.44E + 1	4.53E + 1	3.66%

¹Relative Differnce = $100 * (\text{sample1} - \text{sample2}) / \text{ave}$

8.0 Field, trip, and laboratory spikes and trip blanks

Four laboratory spikes, three trip spikes and three field spikes were analyzed for the application ethoprop test.

8.1 Laboratory spikes

Four laboratory spikes were spiked with 50 ngs of ethoprop on 5/01/98 and stored in the Testing's Laboratory freezer until they were analyzed on 7/14/98. The laboratory spike results are given in Table 17. The average percent recovery was 90% and the relative standard deviation was 5.43%.

Table 17. Laboratory spikes results

Sample Name	Date Spiked	Date Analyzed	Ethoprop Amount (ng/sample)	Amount Ethoprop Spiked (ng/sample)	Percent Recovery
LS01	5/01/98	7/14/98	46.1	50.0	92%
LS01	5/01/98	7/14/98	44.4	50.0	89%
LS02	5/01/98	7/14/98	47.5	50.0	95%
LS03	5/01/98	7/14/98	45.2	50.0	90%
LS04	5/01/98	7/14/98	41.0	50.0	82%

8.2 Trip spikes

A series of 3 trip spikes were spiked with 50.0 ngs of ethoprop on 5/01/98. Trip spikes were taken to the sampling site and returned to laboratory along with a batch of samples, which were analyzed on 5/19/98 and 5/20/98. The trip spike results are given in Table 18. The average recovery was 98% and the relative standard deviation was 8.63%.

Table 18. Trip spike results

Sample Name	Date Spiked	Date Analyzed	Ethoprop Amount (ng/sample)	Amount Ethoprop Spiked (ng/sample)	Percent Recovery
TS01	5/01/98	5/20/98	48.6	50	97%
TS02	5/01/98	5/20/98	43.3	50	87%
TS02	5/01/98	5/20/98	52.8	50	106%
TS04	5/01/98	5/20/98	51.6	50	103%

8.3 Field spikes

A series of 3 field spikes were spiked with 50 ngs of Ethoprop on 5/01/98. Field spikes were taken to the sampling site and ambient air was sampled on the field spikes. An unspiked colocated sample was taken concurrently with the field spikes. The field spike was returned to the laboratory along with a batch of samples. The field spike results are given in Table 19. The average recovery of the

field spikes was 96% with a relative standard deviation of 7.18%.

Table 19. Field spike results

Sample Name	Date Spiked	Date Analyzed	Ethoprop Amount (ng/sample)	Amount Ethoprop Spiked (ng/sample)	Percent Recovery
WFS01	5/01/98	5/19/98	46.5	50.0	93%
SFS02	5/01/98	5/19/98	45.5	50.0	91%
EFS03	5/01/98	5/20/98	51.9	50.0	104%

8.4 Trip blanks

One trip blank was taken to the sampling site and returned to the laboratory with a batch of samples. The trip blank result is given in Table 20.

Table 20. Trip blank results

Sample Name	Date Analyzed	Amount in Sample (ng/sample)
TB03	5/19/98	<MDL

* <MDL = less than the method detection limit

8.5 Backup resin analysis.

The backup resin beds of five samples with the highest ethoprop levels were analyzed for breakthrough. The backup E5BKP contained ethoprop at 5.71 ng/sample. All other backup resin beds were at levels below the MDL. The results are given in Table 21.

Table 21. Backup resin results

Sample Name	Ethoprop Amount (ng/sample)
E5BKP	5.71E+0
E5DBKP	<MDL
S5BKP	<MDL
N5BKP	<MDL
E6BKP	<MDL

* <MDL = Level in sample below the method detection limit

Figure 1. Extracted ion profile of a ethoprop standard at 10 pg/ul at 7.1 times the method detection limit of 1.4 pg/ul.

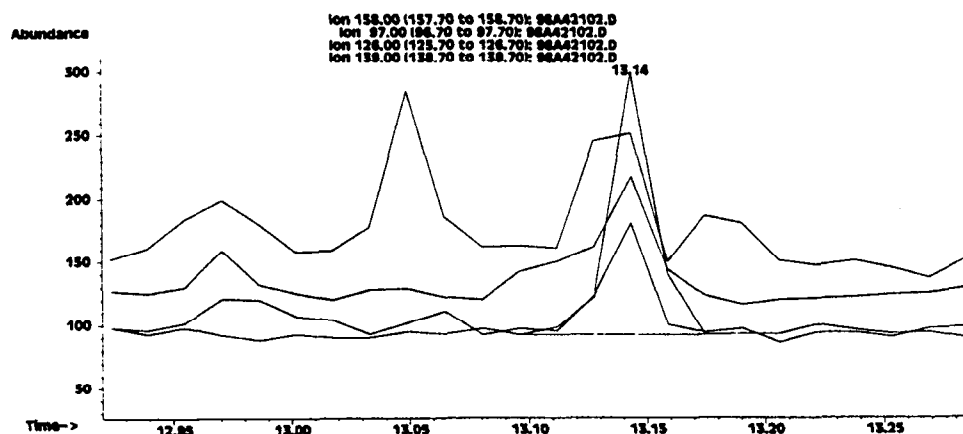


Figure 2. Total ion chromatogram of ambient field spike sample FS01 spiked at 25 pg/ul. The retention time of ethoprop is 12.75 minutes.

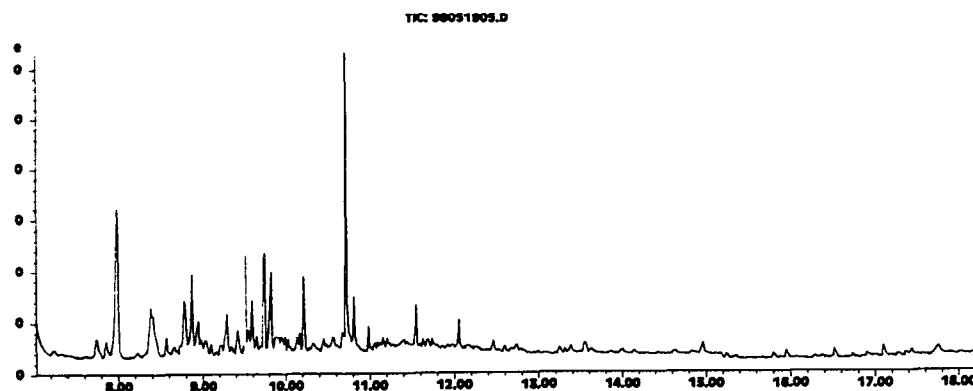


Figure 3. Extracted ion profile of XAD resin blank. No Ethoprop above the detection level was detected. The retention time for ethoprop is 12.75 min.

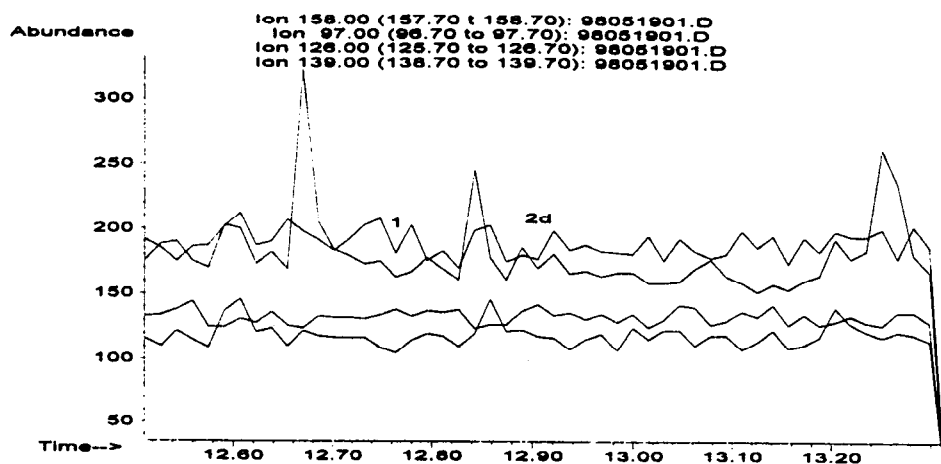
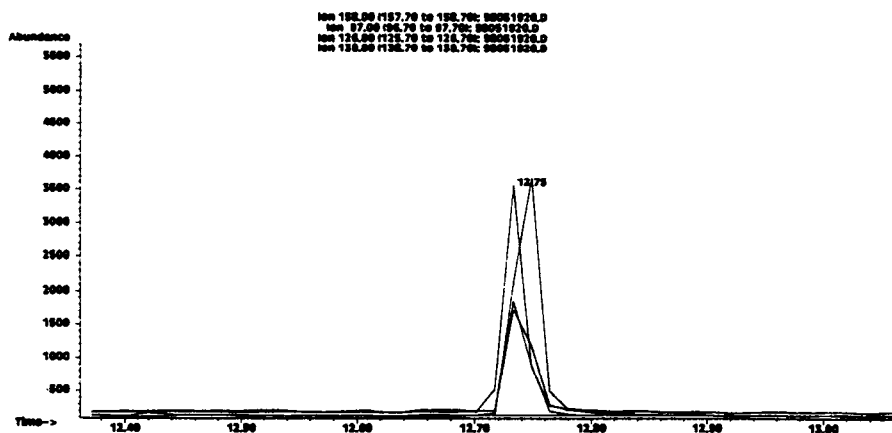


Figure 4. Shown below is sample PAR06 extracted ion profile of ions with m/e of 201, 186 and 173. Ethoprop peak is at 12.75 minutes and the ethoprop concentration is at 30.8 pg/ul.



Attachment One
Ethoprop Standard Operating Procedure

State of California
Air Resources Board
Monitoring and Laboratory Division/ELB

Standard Operating Procedure for the Sampling and
Analysis of Ethoprop in Ambient Air
9/28/98 Version

Analyst: Ken Kiefer and R. Okamoto

Reviewed by: R. Okamoto

Kevin Mongar

1. SCOPE

This is a sorbent tube, solvent extraction, gas chromatography/mass spectrometry method for the determination of ethoprop from ambient air samples.

2. SUMMARY OF METHOD

The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest on dry ice or freezer until desorbed during sonication into 2.5 ml of ethyl acetate. Thirty nanograms of diazinon-D₁₀ internal standard is added to 270 ul of extract prior to analysis. The splitless injection volume is 5 ul. A gas chromatograph with a DB-17 capillary column and a quadrapole mass spectrometer (MS) is used for analysis. The MS detector is operated in selected ion monitoring mode.

3. INTERFERENCES/LIMITATIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. Co-eluting compounds trapped during sample collection may also interfere. A method blank must be analyzed with each batch of samples to detect any possible method interferences.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Hewlett Packard 5890 chromatograph
Hewlett Packard 5971A mass selective detector
Hewlett Packard 8200 autosampler

Detector: 280°C

Injector: 250°C

Injector Liner: Double goose neck liner with glass wool

Column: J&W Scientific DB-17MS, 30 meter, 0.25 mm i.d., 0.25 µm film thickness.

Pre-column: J&W Scientific deactivated fused silica, 2 meter, 0.25 mm i.d.

GC Temp. Program: Initial 50°C, hold 5 min., to 220°C @ 25°C/min., hold 2 min., to 280°C @ 5°C/min., hold 1 min.

Injector:

Pressure Pulse: Initial 6.4 psi, to 40 psi @ 99 psi/min, hold 1.31 min, to 6.4 psi @ 99 psi/min

Splitless: Purge on 2 min.

Gas Flows:

Column: Linear velocity: 32 cm/sec, electronic pressure control (6.4 psi @ 50 °C).

Auto Sampler:

Sample washes - 1, Sample pumps - 4, Sample Volume - 5 stops, Viscosity delay - Zero sec, Solvent A washes - 4, Solvent B washes - 4

Mass Spectrometer:

Electron Ionization

Selective Ion Monitoring; Ethoprop -158 (quant. ion, 100%), 97 (qual. ion, 25%), 126 (qual. ion, 30%), 139 (qual. ion, 35%). Diazinon-D₁₀ - 183 (quant. ion, 100%), 99 (qual. ion, 27%), 304 (qual. ion, 2%)

Tuning: PFTBA

B. AUXILIARY APPARATUS:

1. Glass amber vials, 8 mL capacity.
2. Glass amber vials, 4 mL capacity.
3. Vial Shaker, SKC, or equiv.
4. Sonicator, Branson 2210
5. Autosampler vials with septum caps.

C. REAGENTS

1. Ethyl Acetate, Pesticide Grade, or better
2. Ethoprop, 99% pure or better (e.g., from Chem Service).
3. Diazinon-D₁₀ 99% pure or better (e.g., from Cambridge Isotope Laboratories)

5. ANALYSIS OF SAMPLES

1. A daily manual tune shall be performed using PFTBA. The instrument is tuned using masses - 69, 219, 502. The criterion for the peak widths at 1/2 the peak height is $0.5 \pm .05$. The criteria for relative abundances are; 69 - 100%; 219 - 60-70%; and 502 - 2-5%.
2. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample, which results in possible carry-over contamination.
3. A 5-point calibration curve shall be analyzed with each batch of samples. A single point calibration check at the midpoint of the calibration curve may be substituted for the 5 point calibration curve provided that it is within 20% of the average response factor from an initial 5 point multi-point calibration curve and the calibration updated. Then a second midpoint calibration standard is run. If both midpoint calibrations are within 20% of each other then analysis of batch samples can proceed.
4. With each batch of samples a laboratory blank and two laboratory check samples will be run. A laboratory blank is a blank resin cartridge prepared and analyzed the same way the samples are analyzed. A laboratory check sample is a resin cartridge spiked with a known amount of standard. The check sample is prepped and analyzed the same way as the samples. Laboratory check samples need to be within 20% ($100 \times \text{difference/average}$) of each other and have recoveries that are $\pm 30\%$ of the theoretical spiked value.
5. At least one calibration check sample must be analyzed for each batch of ten samples. The response of the standard must be within 20% of the initial calibration analyses for the batch. If the calibration check is outside the limit then those samples in the batch after the last calibration check that was within the 20% limit need to be reanalyzed.
6. Carefully score the secondary section end of the sampled XAD-2 tube above the glasswool and break at the score. Remove the glass wool plug from the secondary end of the XAD-2 tube with forceps and place it into a 4 mL amber colored sample vial. Pour the backup portion of the XAD-2 into the same vial.
7. Pour the primary XAD into an 8 ml vial. Remove the glasswool plug and put it into the 8 ml vial. Rinse the tube with 2.5 ml of ethyl acetate and pour rinse into the 8 ml vial.

8. Place the sample vial on a desorption shaker (or ultra sonic water-bath) for 30 minutes. Remove the ethoprop extract and store in a second vial at - 20°C until analysis.
9. Add a 270 ul aliquot of the sample extract to the autosampler vial. Spike the sample extract with 30ul of 1000 pg/ul diazinon-D₁₀.
10. After calibration of the GC system, inject 5.0 ul of the extract. If the resultant peak for ethoprop has a measured concentration greater than that of the highest standard injected dilute the sample and re-inject.
11. Calculate the concentration in ng/mL based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.
12. The atmospheric concentration is calculated according to:

$$\text{Conc., ng/m}^3 = (\text{Extract Conc., ng/mL} \times 2.5 \text{ mL}) / \text{Air Volume Sampled, m}^3$$

6. QUALITY ASSURANCE

A. INSTRUMENT REPRODUCIBILITY

Five injections of 5 ul each were made of ethoprop standards at three concentrations in order to establish the reproducibility of this instrument. This data (Testing Section lab, 12/11/97) is shown in Table 1.

TABLE 1. Instrument Reproducibility

Diazinon-D ₁₀ Conc. (ng/ml)	Diazinon-D ₁₀ Response	Ethoprop Conc. (ng/ml)	Ethoprop Response	Amt. Ratio	Resp Ratio	Response Ratio RSD
100	2743	12.5	582	.125	.212	5.92
100	2544	12.5	581	.125	.228	
100	2757	12.5	624	.125	.226	
100	2691	12.5	673	.125	.250	
100	2544	12.5	581	.125	.228	
100	2628	50	2564	.50	.976	3.84
100	2454	50	2533	.50	1.03	
100	2491	50	2573	.50	1.03	
100	2467	50	2601	.50	1.05	
100	2165	50	2347	.50	1.08	
100	2972	250	16325	2.5	5.49	3.06
100	2781	250	16322	2.5	5.87	
100	2650	250	15798	2.5	5.96	
100	2089	250	12040	2.5	5.76	
100	2877	250	16498	2.5	5.73	

B. CALIBRATION

Initial Calibration

Linearity

A linear regression was performed on a 12.5 pg/ul-200 pg/ul 5-point calibration curve made on 12/11/97.

$$\text{Resp Ratio} = (2.18) * (\text{amount ratio}) - 6.65e^{-2}$$

$$R^2 = .999$$

A linear regression was also performed on a 2 pg/ul-32 pg/ul 4-point multi-point calibration curve made on 4/21/98.

$$\text{Resp Ratio} = (1.36) * (\text{amount ratio}) - 4.76e^{-2}$$

$$R^2 = 1.000$$

C. MINIMUM DETECTION LIMIT

Detection limit is based on USEPA detection limit calculation. Using the analysis of seven replicates of low level matrix spikes, the method detection limit (MDL), and the estimated quantitation limit (EQL) for ethoprop were calculated by:

$$\text{MDL} = 3.14 * s$$

$$\text{EQL} = 5 * \text{MDL}$$

where:

s = the standard deviation of the concentration calculated for the seven replicate spikes.

Given s = .1206 ng/ml for the seven samples, the MDL and EQL are calculated as follows.

$$\text{MDL} = 3.14 * .121 = .379 \text{ pg/ul}$$

$$\text{EQL} = 5 * .379 = 1.89 \text{ pg/ul}$$

Based on the 2.5 mL extraction volume and assuming a sample volume of

4.32 m³ (3 lpm for 24 hours) the ambient concentration of ethoprop at the EQL is:

$$(1.89 \text{ ng/mL})(2.5 \text{ mL}) / (4.32 \text{ m}^3) = 1.09 \text{ ng/m}^3 \text{ per 24-hour sample}^1$$

¹The reported MDL and EQL were obtained by spiking the resin with 10 ngs of ethoprop standard, calibrating the samples with a low level calibration curve, and by increasing the MS electron multiplier voltage. This resulted in an approximately eight-fold lower detection limit than using the high concentration spikes and calibration curve.

D. COLLECTION AND EXTRACTION EFFICIENCY (RECOVERY)

62.5 ng of ethoprop standard was spiked on the primary section of each of six XAD-2 sampling tubes. The spiked tubes were then subjected to an airflow of 3 lpm for 24 hours. The samplers were set-up at 13th and T St. in Sacramento at an ambient temperature of approximately 30°C (maximum). The primary sections were then extracted with ethyl acetate and analyzed. Percent recoveries of ethoprop from primary sections of three tubes analyzed within one week of sampling were 64.8%, 61.7%, 62.3% with an average of 62.9% and the percent recoveries of three tubes analyzed within two weeks of sampling were 56.6%, 60.9%, and 67.8 with an average of 61.7%. In the initial validation study suggest that the recovery of cartridges spiked at levels near the EQL and subjected to field conditions may be 50% or less.

E. STORAGE STABILITY

Storage stability studies were conducted over a 4-week period. The primary sections of 19 tubes were spiked with 62.5 ng of Ethoprop. The spiked tubes were stored in the freezer at -20°C and extracted/analyzed on storage weeks 1,2,3 and 4. Four tubes were analyzed on week 1 and 5 tubes each were analyzed on weeks 2, 3, and 4. The storage recoveries (average results) were 79.1%, 81.9%, 64.7% and 77.3% for weeks 1,2,3 and 4 respectively.

A second set of fifteen tubes was spiked with 1250 ngs of Ethoprop. The spiked tubes were stored in the freezer at -20°C and extracted/analyzed on storage weeks 1, 3 and 4. Five tubes each were analyzed on week 1, 3, and 4. The storage recoveries (average results) were 97.8%, 75.2%, and 91.9% respectively.

F. BREAKTHROUGH

The primary sections of four tubes were spiked with 62.5 ng ethoprop/tube then run for 24 hours at 3 lpm (see Section D above). No ethoprop was detected in the back-up resin bed of any of the tubes.

G. Safety

Ethoprop is highly toxic if inhaled, moderately toxic if ingested, and slightly toxic via dermal exposure. The LD₅₀ ranges is 16.7 mg/kg/day for rats. The 4-hour inhalation LC50 in rats is .136 mg/L for male rats and .002 mg/L for female rats. The TWA is .1 mg/m³.

APPENDIX III
PESTICIDE USE REPORT

STATE OF CALIFORNIA

PRODUCTION AGRICULTURE MONTHLY PESTICIDE USE REPORT: MULTIPLE SECTION

108567

DEPARTMENT OF PESTICIDE REGULATION
PESTICIDE ENFORCEMENT BRANCH

1. MONTH <i>June</i>	2. YEAR <i>1998</i>	3. COUNTY NO. <i>47</i>
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TO Kevin Monger
FROM Siskiyou Co Ag

4. COMMODITY / SITE TREATED <i>SEE BELOW UNDER INDIVIDUAL SITE ID</i>	5. OPERATOR ID / PERMIT NO. <i>47-96-473923 A</i>	6. OPERATOR (GROWER) <i>Wheeler Farms</i>	7. ADDRESS <i>P. O. Box 10</i>	8. CITY <i>Macdonald, CA</i>	9. ZIP CODE <i>96058</i>
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10. SECTION	11. TOWNSHIP	12. RANGE	13. BASE AND MERIDIAN	14. SITE IDENTIFICATION NUMBER	15. DATE AND TIME APPLICATION COMPLETED	16. TOTAL PLANTED ACRES	17. TOTAL TREATED ACRES	18. APP. METHOD	19. EPA / CALIF. REG. NO. FROM LABEL	20. TOTAL PRODUCT USED LB OZ PT QT GA	21. RATE PER ACRE	22. DILUTION	23. DAYS REENTRY	24. MANUFACTURE / NAME OF PRODUCT
24	48N	02W	N	WF-05 POTATO	6/98	155	155	GP	264-485	5000.00 0 0 0 0 100				Mocap 10 G Rhône Poulenc
24	48N	02W	N	WF-05 POTATO	5/98	155	155	OTHER	7501-157	508.67 0 0 0 0 0.73333				Tops MZ Gustafson
36	46N	02W	N	WF-07 POTATO	5/98	80	80	GP	10182-220-AA	0.00 0 0 160 0 2				Eptam 7-E Zeneca
36	48N	02W	N	WF-07 POTATO	5/98	80	80	GP	264-485	4000.00 0 0 0 0 100				Mocap 10 G Rhône Poulenc
46	46N	02W	N	WF-07 POTATO	5/98	80	80	OTHER	7501-157	778.67 0 0 0 0 0.73333				Tops MZ Gustafson
2	48N	01W	N	WF-08 POTATO	5/98	80	80	GP	10182-220-AA	0.00 0 0 160 0 2				Eptam 7-E Zeneca
2	46N	01W	N	WF-08 POTATO	5/98	80	80	OTHER	264-485	4000.00 0 0 0 0 100				Mocap 10 G Rhône Poulenc
2	46N	01W	N	WF-08 POTATO	5/98	80	80	OTHER	7501-157	778.67 0 0 0 0 0.73333				Tops MZ Gustafson
				WF-07	5/98			GP	264-485	4000.00 0 0 0 0 100				Mocap 10 G Rhône Poulenc

RECEIVED

REPORT PREPARED BY

Danni Tonelli

DATE

6/16/98

JUN 23 1998

SISKIYOU COUNTY DEPT. OF AGRICULTURE
TULSELAND

FOR AGENCY USE ONLY

APPENDIX IV

DPR's
AIR MONITORING RECOMMENDATIONS FOR ETHOPROP

M e m o r a n d u m

To: George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division
Air Resources Board
600 North Market Boulevard
Sacramento, California 95812

Date: July 24, 1997

From: Department of Pesticide Regulation - 1020 N Street, Room 161
Sacramento, California 95814-5624

Subject: AIR MONITORING RECOMMENDATION FOR ETHOPROP

Attached is the Department of Pesticide Regulation's (DPR) recommendation for monitoring the organophosphate pesticide ethoprop. DPR provides this recommendation pursuant to the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5). DPR bases its air monitoring recommendations on historical ethoprop use information. Therefore, we request you consult with the agricultural commissioner in the county where air monitoring will be conducted to select appropriate sites.

We anticipate submission of air monitoring data by January 1999.

If you have any questions please contact Pam Wales, of my staff, at (916) 322-3877.



John S. Sanders, Chief
Environmental Monitoring and
Pest Management Branch
(916) 324-4100

Attachment



Chief George Lew

July 24, 1997

Page 2

cc: Pam Wales, DPR (w/attachment)
Madeline Brattesani, DPR (w/attachment)
Charles M. Andrews, DPR (w/attachment)
Barry Cortez, DPR (w/attachment)
John Donahue, DPR (w/attachment)
Gary Patterson, DPR (w/attachment)
Lynn Baker, ARB (w/attachment)
Cindy Castronovo, ARB (w/attachment)
Raymond Menebroker, ARB (w/attachment)
Kevin Mongar, ARB (w/attachment)
James R. Massey, Jr, Agricultural Commissioner Siskiyou County (w/attachment)



Staff Report

USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDE ACTIVE INGREDIENT ETHOPROP

July 1997

Principal Author
Pamela Wales
Environmental Research Scientist

Graphics by
Craig Nordmark
Environmental Research Scientist

State of California
Department of Pesticide Regulation
1020 N Street
Sacramento, California 95814-5624

USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDE ACTIVE INGREDIENT ETHOPROP

A. BACKGROUND

This recommendation contains general information regarding the physical-chemical properties and the historical uses of the organophosphate pesticide *O*-Ethyl *S,S*-dipropyl phosphorodithioate (ethoprop). The Department of Pesticide Regulation (DPR) provides this information to assist the Air Resources Board (ARB) in their selection of appropriate locations for conducting pesticide air monitoring operations.

Ethoprop (CAS: 13194-48-4) exists as a clear, pale yellow liquid. Ethoprop has a molecular formula of $C_8H_{19}O_2PS_2$, and a molecular weight of 242.33 g/mole. It has a water solubility of 700 mg/L at 20 °C, a Henry's Constant of 1.59×10^{-7} atm·m³/mol at 20–25 °C, and a vapor pressure of 3.49×10^{-4} mmHg (46.5 mPa) at 20 °C. Ethoprop is miscible with acetone, *n*-hexane, and xylene.

The reported half-lives in humus-containing soil (pH 4.5) and a sandy loam (pH 7.2-7.3) were 87 and 14-28 days, respectively. Accelerated transformation of ethoprop after repeated soil applications was reported. When heated to decomposition, ethoprop emits toxic phosphorus and sulfur oxide fumes.

Ethoprop's acute oral LD₅₀ is 262 mg/kg for rats. Its LC₅₀ (96 hour) is 13.8 mg/L for rainbow trout, 2.1 mg/L for bluegill sunfish, and 13.6 mg/L for goldfish. Ethoprop entered the risk assessment process at DPR under SB 950 (Birth Defect Prevention Act of 1984) based on potential combined oncogenicity and chronic toxicity and mutagenic effects.

B. USE OF ETHOPROP

As of July 1, 1997, five ethoprop-containing products (Mocap®[†]) were registered for use in California. Ethoprop is a systemic, nonfumigant soil-applied nematicide-insecticide, used to control a variety of nematodes and insect pests. Ethoprop has a low volatility and can be applied before or after planting until immediately prior to crop emergence. DPR regulates ethoprop as a restricted use pesticide when it is used for the production of agricultural plant commodities. Restricted use pesticides may be possessed and used only by certified applicators who have obtained a special permit from their county agricultural commissioner.

[†] Mocap® is the registered brand name for ethoprop-containing products. Mocap is a registered tradename of the Rhône-Poulenc Ag Company, P.O. Box 12014, 2 T.W. Alexander Drive, Research Triangle Park, NC 27709.

With DPR's implementation of full pesticide use reporting in 1990, all users must report the agricultural use of any pesticide to their county agricultural commissioners, who subsequently forward this information to DPR. DPR compiles and publishes the use information in the annual Pesticide Use Report (PUR). Because of California's broad definition for agricultural use, DPR includes data from pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and rights-of-way, postharvest applications of pesticides to agricultural commodities, and all pesticides used in poultry and fish production, and some livestock applications in the PUR. DPR does not collect use information for home and garden use, or for most industrial and institutional uses. The information included in this monitoring recommendation reflects cropland applications of ethoprop. Use rates were calculated by dividing the total pounds of ethoprop reported used (where ethoprop was applied to acreage) by the total number of acres reported treated.

According to the PUR, over 99 percent of California's total ethoprop use occurs in ten counties (Table 1). Historically, cropland applications account for over 97 percent of the total amount of ethoprop reported used each year. Non-agricultural applications—landscape maintenance—account for less than one percent of the total amount of ethoprop reported used each year.

In California, growers use ethoprop to control a variety of nematodes and wireworms in potatoes. Labeled use rates for ethoprop range from 3 to 12 pounds active ingredient (AI) per acre in potatoes. The higher rates of use are associated with moderate to severe infestations of nematodes or wireworms. Ethoprop is also used to control insects and nematodes in sweet potatoes and cabbage, but at much lower rates (1.5 to 6 pounds AI per acre). Ethoprop is formulated in either granular/flake form or as a ready-to-use liquid solution. Ethoprop-containing products include the Signal Word "Warning" or "Poison/Danger" on their labels, depending on the formulation or concentration of the product.

Table 1. Annual Agricultural Use of Ethoprop (Pounds of Active Ingredient)

COUNTY	1995	1994	1993
Siskiyou	26,014	20,158	22,177
San Joaquin	11,494	6,736	4,701
Modoc	9,116	11,270	14,380
Monterey	4,925	2,223	6,738
Santa Barbara	1,348	1,206	714
Amador	1,268	0	0
Riverside	1,321	313	494
San Luis Obispo	1,018	1,042	920
Kern	761	5,951	4,359
Merced	569	1,702	5,535
County Totals	57,834	50,601	60,018
Percent of Total	>99%	99%	97%
CALIFORNIA TOTAL	57,936	51,270	62,143

According to the PUR, Siskiyou County routinely receives the greatest applications of ethoprop; where growers apply nearly 40 percent of all the ethoprop used. Table 2 summarizes the total amounts and average daily rates of ethoprop reported applied in Siskiyou County during the months of greatest use. In Siskiyou County, reported applications of ethoprop are highest from mid-April through May and are associated with application to potatoes in the northeastern area of the County. Generally, growers use the granular formulation, applying before planting and immediately incorporating into the soil. The second highest reported use occurs in San Joaquin County in April; however, the amounts are half of those reported for Siskiyou County, and applications are scattered throughout the County.

Table 2. Ethoprop Applications in Siskiyou County

MONTH	1995		1994		1993	
	Lbs Used ¹	Rate ²	Lbs Used ¹	Rate ²	Lbs Used ¹	Rate ²
May	18,265	12.3	7,459	7.4	16,389	9.1
April	7,749	10.8	12,602	10.2	4,094	10.3

¹ In pounds of active ingredient.

² Average rate (in pounds of active ingredient per acre).

The highest reported rates of ethoprop use average 12 lbs AI per acre (the highest labeled rate), and are associated with applications to potatoes.

C. RECOMMENDATIONS

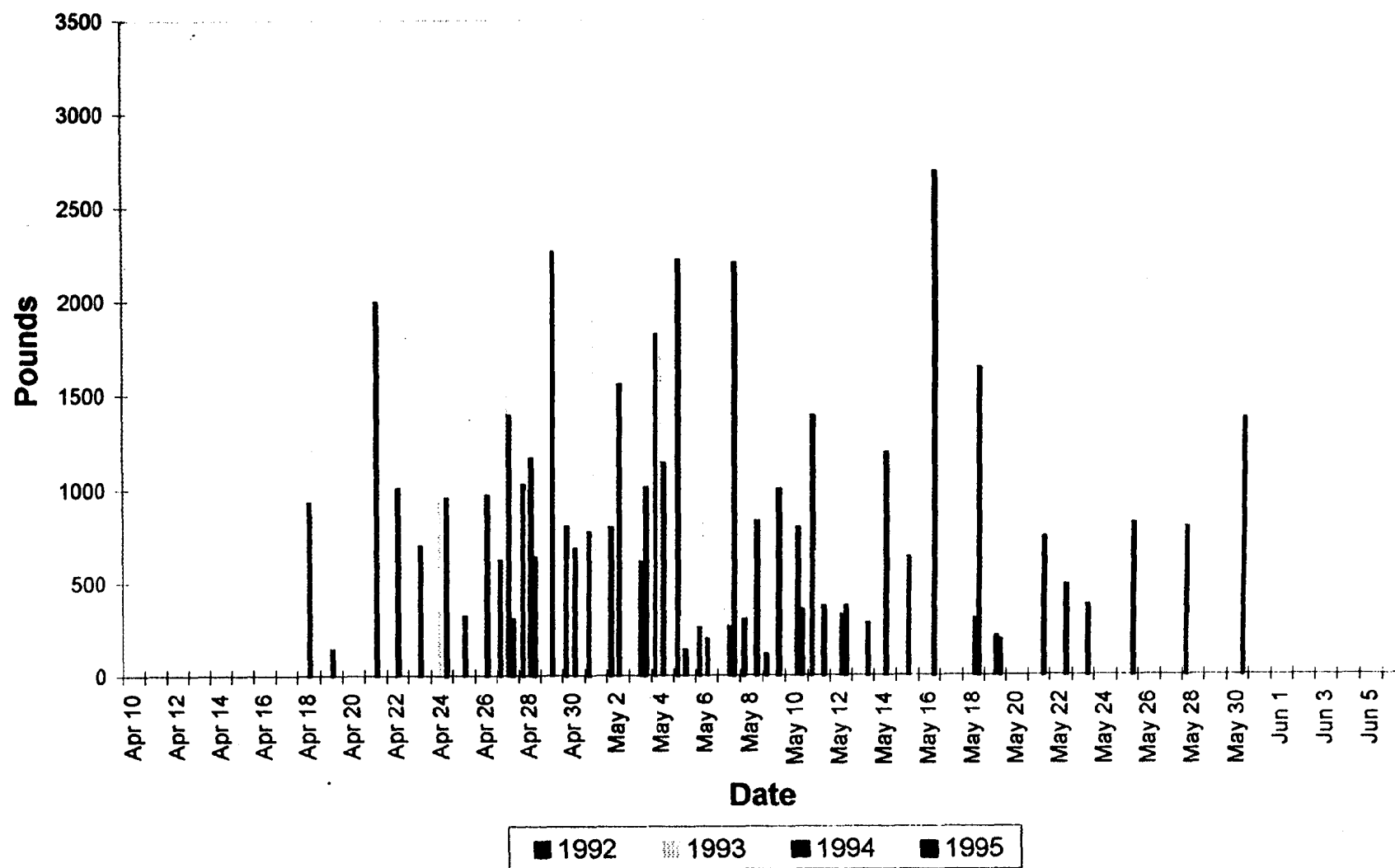
1. *Ambient Air Monitoring*

The historical trends in ethoprop use suggest that monitoring should occur over a 30- to 45-day sampling period in the northeastern region of Siskiyou County from mid-April through May. Figure 1 shows applications routinely begin in mid-April, reach a peak during the last week in April and the first two weeks in May, then tail off throughout the remainder of the month. Figure 2 displays the areas of ethoprop use by section in northeastern Siskiyou County for 1994-1995. Figure 3 shows the same information for 1992-1993. Ethoprop is generally applied within two weeks before planting or before crop emergence. Severe weather conditions may affect the time of planting. Furthermore, this area is very close to Oregon potato growing regions. Care should be taken to prevent applications of ethoprop to nearby Oregon potato fields from contaminating collected samples. Because ethoprop is a restricted material, the county agricultural commissioner must issue a permit to each user before it is applied. These permits include information such as application site locations. For these reasons, DPR strongly recommends close coordination with the county agricultural commissioner to select the best sampling sites and periods.

Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be located near potato growing areas. Ambient samples should not be collected from samplers immediately adjacent to fields or orchards where ethoprop is being applied. At each site, twenty to thirty discrete 24-hour samples should be taken during the sampling period. Background samples should be collected in an area distant to ethoprop applications.

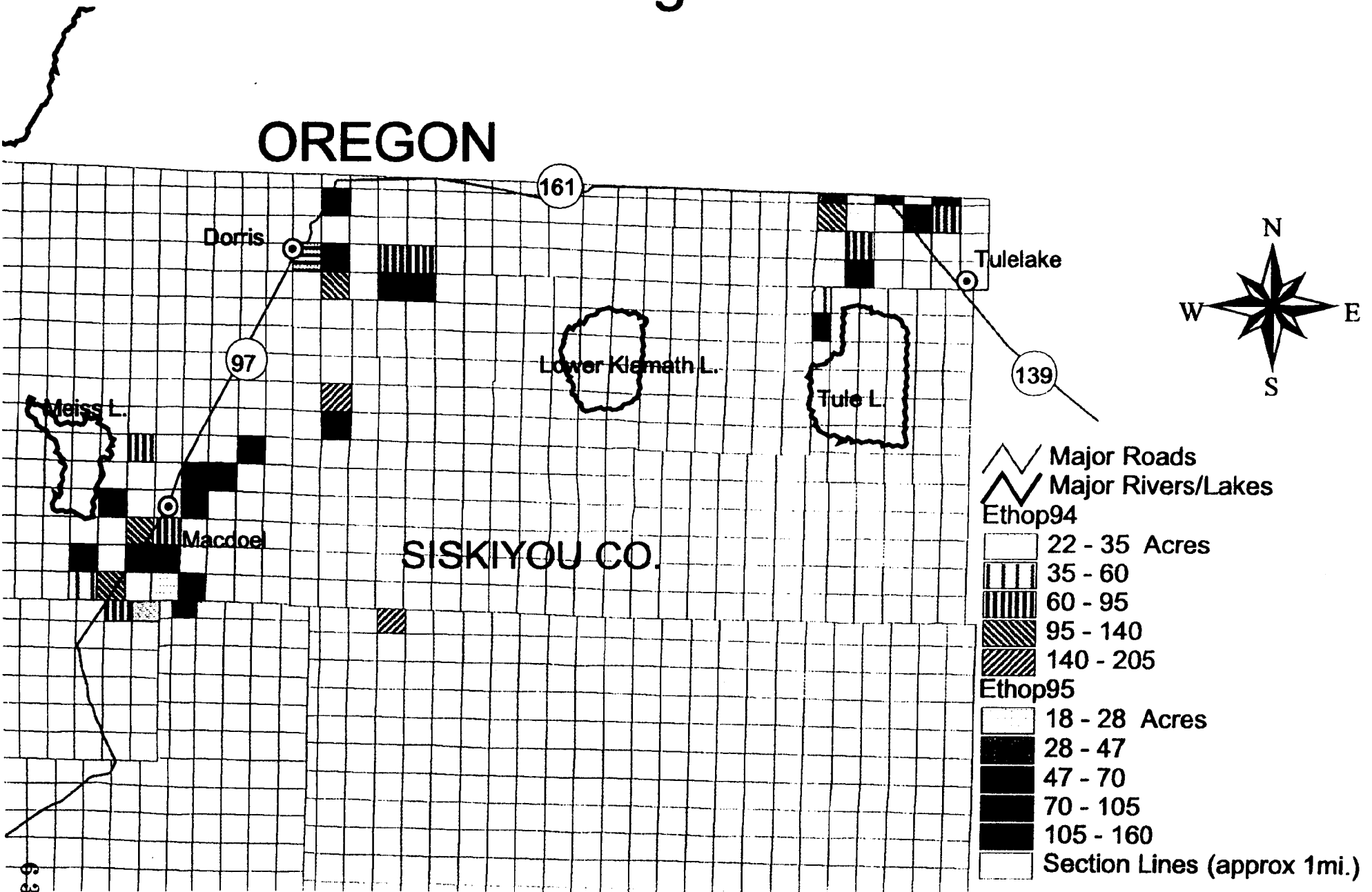
Replicate (collocated) samples are needed for five dates at each sampling location. Two collocated samplers (in addition to the primary sampler) should be run on those days. The date chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site. Trip blank and field spike samples should be collected at the same environmental conditions (e.g., temperature, humidity, exposure to sunlight) and experimental conditions (e.g., air flow rates) as those occurring at the time of ambient sampling.

Figure 1. Applications of Ethoprop to Potatoes in Northeastern Siskiyou County (1992-1995)



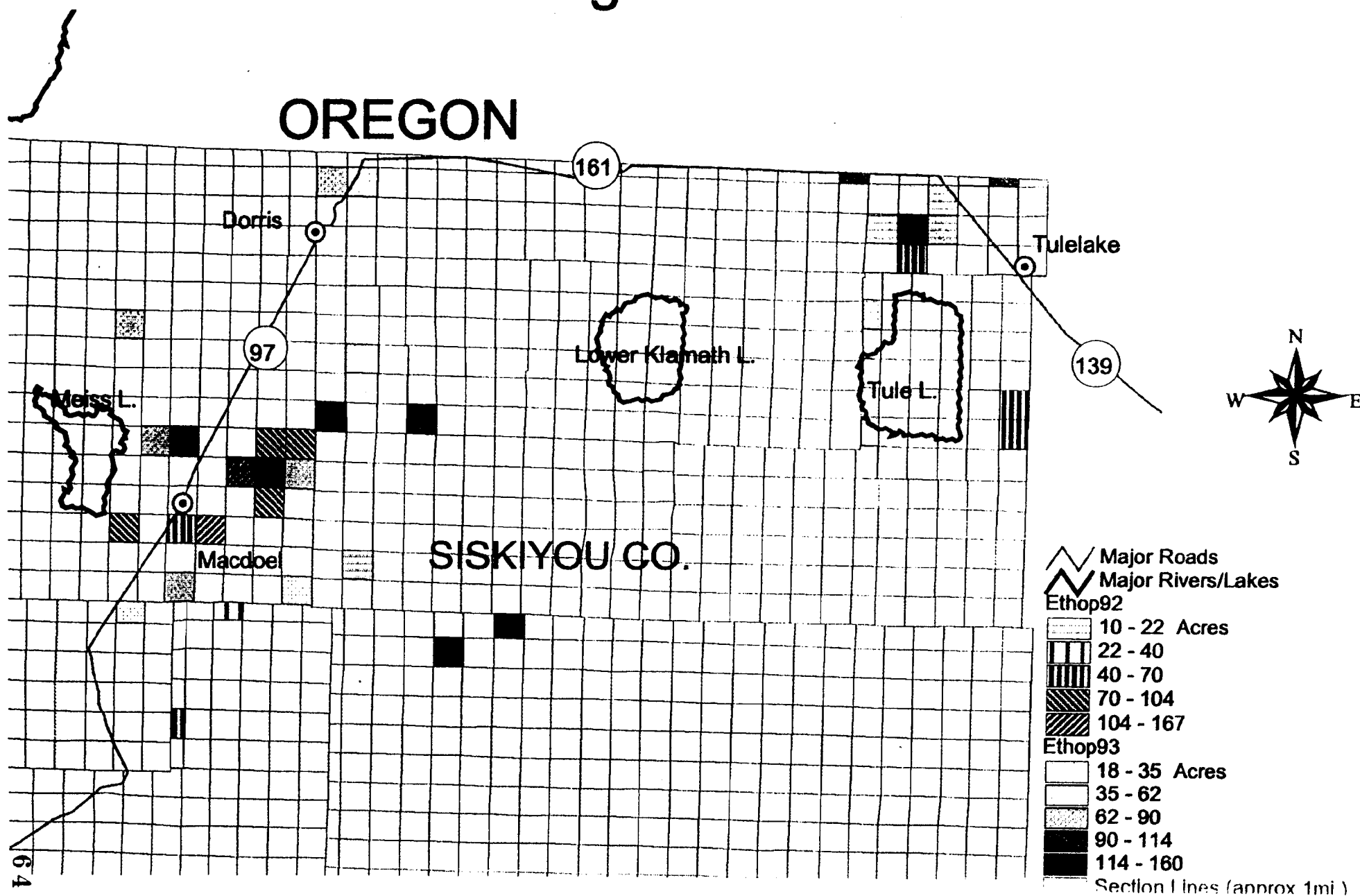
Ethoprop Applications in Siskiyou Co. 1994-95

Figure 2



Ethoprop Applications in Siskiyou Co. 1992-93

Figure 3



2. Application-Site Air Monitoring

The historical trends in ethoprop use suggest that application-site air monitoring should also be conducted from mid-April through May in northeastern Siskiyou County in association with application to potatoes. Monitoring should occur at a site of highest rate of use—12 pounds AI per acre. Because the degree of nematode infestation—and thus, the rate of ethoprop use—may vary from location to location, DPR recommends close coordination with the county agricultural commissioner to select the best sampling sites. Ethoprop is intensively applied during this period so care should be taken to prevent nearby applications from contaminating collected samples. Again, care should be taken to prevent applications of ethoprop to nearby Oregon potato fields from contaminating collected samples.

A three day monitoring period should be established with sampling times as follows: application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples and two 24-hour samples. A minimum of four samplers should be positioned, one on each side of the field. A fifth sampler should be collocated at one position. Since ethoprop is extensively used in the area, background samples should collect enough volume (either 12 hours at 15 liters/min, or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. Ideally, samplers should be placed a minimum of 20 meters from the field. Trip blank and field spike samples should be collected at the same environmental conditions (temperature humidity, exposure to sunlight) and experimental conditions (similar air flow rates) as those occurring at the time of sampling.

Additionally, we request that you provide in the monitoring report: 1) an accurate record of the positions of the monitoring equipment with respect to the field, including the exact distance that the sampler is positioned from the field; 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles; 3) meteorological data collected at a minimum of 15-minute intervals including wind speed and direction, humidity, and air temperature, and comments regarding degree of cloud cover; and 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North).

D. SAFETY RECOMMENDATIONS

A cholinesterase inhibitor, ethoprop is rapidly absorbed through the skin, and became a restricted use pesticide because of its acute dermal toxicity. The symptoms of poisoning may include nausea, vomiting, abdominal cramps, diarrhea, excessive salivation, headache, dizziness, weakness, blurring or dimness of vision, excessive tearing, loss of muscular coordination, slurring of speech, twitching of muscles (especially of the tongue

and eyelids), mental confusion, disorientation, drowsiness, tightness in the chest, and runny nose.

Therefore, monitoring personnel should use proper protective equipment if there is a possibility of exposure to breathing the fumes, or spray mist (if liquid formulation used). According to the label, proper equipment for applicators includes Tyvek[®] coveralls over long-sleeved shirt and long pants, chemical resistant gloves (such as disposable nitrile rubber), chemical resistant footwear plus socks, protective eyewear, and a cartridge respirator equipped with a filter cartridge approved for use with organophosphate pesticides. The restricted entry interval following ethoprop application is 48 hours. The interval is increased to 72 hours in outdoor areas where average rainfall is less than 25 inches per year. Monitoring personnel should read and refer to the label of the actual product used for further precautions.

E. REFERENCES

- Kelley, K. and N.R. Reed. 1996. Pesticides for evaluation as candidate toxic air contaminants. Department of Pesticides Regulation. Sacramento, California. Report No. EH 96-01.
- Montgomery, J.H. 1993. Agrochemicals Desk Reference: Environmental Data. Lewis Publishers, Chelsea, Michigan.

APPENDIX V

APPLICATION AND AMBIENT FIELD LOG SHEETS

MacDoel Elementary School (MAC)
Doris Elementary School (DOR)

Newell Elementary School (NE)
Tule Lake Bus Barn (TL)

LOG BOOK

Project: Ethnopro Ambient in Siskiyou Co.
Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by	
1	MAC 1	4/28/88	1000	14 ft off ground ^{parmy} (29) + 28	K	NEW
2	DOR 1	4/28	1030	10A + 10B		
3	TLB 1	4/28	0915	8A 8B		
4	NEW 1	4/28	1220	9A 9B		
5	LAV 1	4/29	1225	11A 11B		
6	LAV10	4/29	1315			
7	MAC2	4/29	0835			
8	DOR2	4/30	1121			
9	TLB2	4/29	0915			
10	NEW2	4/30	1100			
11	LAV2	4/29	0950			
12	LAV20	4/30	0945			
13	MAC3	4/29	1147			
14	DOR3	4/30	0925			
15	TLB3	4/29	1225			
16	NEW3	4/30	0835			
17	LAV3	4/30	0835			
18	LAV30	5/1	0735			
19	B3	5/1	1015	Blank		

MAC-4
DOR
TLB
NEW
LAV

LOG BOOK

Project: Ethoprop Ambient in Siskiyou Co.

Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by	
19	B3	5/1	1015	Blank		
20	LAV4	5/4 5/5	1120 0935		o	MA
21	FS1	5/4 5/5	1120 0935	#12		
22	FS2	5/4 5/5	1120 0935	#13		
23	NEW4	5/4 5/5	1205 1035			
24	TLB4	5/4 5/5	1225 1050			
25	DOR4	5/4 5/5	1335 1205			
26	MAC4	5/4 5/5	1415 1235			
27	LAV5	5/5 5/6	0935 0900			
28	FS3	5/5 5/6	0935 0900			
29	FS4	5/5 5/6	0935 0900	#12		
30	FS5	5/5 5/6	0935 0900	#13		
31	NEW5	5/5 5/6	1035 0945			
32	TLB5	5/5 5/6	1050 1010			
33	D045	5/5 5/6	1205 1110			
34	MAC5	5/5 5/6	1235 1135			
35	LAV6	5/6 5/7	0900 0850			
36	LAV6D	5/6 5/7	0900 0850			
37	NEW6	5/6 5/7	0945 0940			
38	NEW6D	5/6 5/7	0945 0940			
39	TLB6	5/6 5/7	1010 1005			
40	TLB6D	5/6 5/7	1010 1005			

LOG BOOK

Project: Ethoprop Ambient in Siskiyou Co.

Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
41	DOR6	5/16	1110		o/pc ↓	
		5/17	1105			
42	DOR6D	5/16	1110			
		5/17	1135			
43	MAC6	5/16	1140			
		5/17	1135			
44	MAC6D	5/16	1140			
		5/17	1135			
45	LAV7	5/17	0850			
		5/18	0815			
46	NEW7	5/17	0940		↓	
		5/18	0910			
47	TLB7	5/17	1005			
		5/18	0935			
48	DOR7	5/17	1105			
		5/18	1015			
49	MAC7	5/17	1135			
		5/18	1100			
50	BLANK	5/18		BA		
51	TS1		1800		↓	
52	TS2					
53	TS3					
54	TS4					
55	TS5					
56	LAV8	5/11/98	1230			
		5/12/98	0855			
57	NEW8	5/11	1315			HEM
		5/12/98	0940			LUT
58	TLB8	5/11	1330			
		5/12/98	1000		↓	
59	DOR8	5/11	1410			
		5/12/98	1115			
60	MAC8	5/11	1430			
		5/12/98	1136			
61	LAV9	5/12/98	0855			
		5/13/98	0920			
62	NEW9	5/12/98	0940			
		5/13/98	1035			

LOG BOOK

Project: Ethoprop Ambient in Siskiyou Co.

Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by
63	TLB 9	5/12/98	1000		
		5/13/98	1045		
64	DOR 9	5/12/98	1115		
		5/13/98	1155		
65	MAC 9	5/12/98	1136		
		5/13/98	1212		
66	LAV 10	5/13/98	0920		
		5/14/98	0935		
67	LAV 10D	5/13/98	0920		
		5/14/98	0935		
68	NEW 10	5/13/98	1025		
		5/14/98	1025		
69	NEW 10D	5/13/98	1025		
		5/14/98	1025		
70	TLB 10	5/13/98	1045		
		5/14/98	1045		
71	TLB 10D	5/13/98	1045		
		5/14/98	1045		
72	DOR 10	5/13/98	1155		
		5/14/98	1157		
73	DOR 10D	5/13/98	1155		
		5/14/98	1157		
74	MAC 10	5/13/98	1212		
		5/14/98	1222		
75	MAC 10D	5/13/98	1212		
		5/14/98	1222		
76	LAV 11	5/14/98	0935		
		5/15/98	0815		
77	NEW 11	5/14/98	1025		
		5/15/98	0900		
78	TLB 11	5/14/98	1045		
		5/15/98	0915		
79	DOR 11	5/14/98	1157		
		5/15/98	1005		
80	MAC 11	5/14/98	1222		
		5/15/98	1025		
81	BLANK	5/14/98	1222	TAKEN AT MAC SITE	
		—	—		
82	MAC 12	5/18/98	1230		
		5/19/98	1205		
83	DOR 12	5/18/98	1300		
		5/19/98	1145		
84	LAV 12	5/18/98	1415		
		5/19/98	0945		

LOG BOOK

Project: Ethoprop Ambient in Siskiyou Co.
Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by
85	NEW 12	5/18/98	1455		JJS
		5/19/98	1045		
86	TLB 12	5/19/98	1515		/
		5/19/98	1100		
87	LAV 13	5/14/98	0945		
		5/20/98	0935		
88	NEW 13	5/14/98	1045		
		5/20/98	1015		
89	TLB 13	5/14/98	1100		
		5/20/98	1035		
90	DOR 13	5/19/98	1145		
		5/20/98	1135		
91	MAC 13	5/19/98	1205		
		5/20/98	1210		
92	LAV 14	5/20/98	0935		
		5/21/98	0935		
93	LAV 14D	5/20/98	0935		
		5/21/98	0935		
94	NEW 14	5/20/98	1015		
		5/21/98	1015		
95	NEW 14D	5/20/98	1015		
		5/21/98	1015		
96	TLB 14	5/20/98	1035		
		5/21/98	1035		
97	TLB 14D	5/20/98	1035		
		5/21/98	1035		
98	DOR 14	5/20/98	1135		
		5/21/98	1115		
99	DOR 14D	5/20/98	1135		
		5/21/98	1115		
100	MAC 14	5/20/98	1210		
		5/21/98	1135		
101	MAC 14D	5/20/98	1210		
		5/21/98	1135		
102	LAV 15	5/21/98	0935		
		5/22/98	0750		
103	NEW 15	5/21/98	1015		
		5/22/98	0825		
104	TLB 15	5/21/98	1035		
		5/22/98	0845		
105	DOR 15	5/21/98	1115		
		5/22/98	0920		
106	MAC 15	5/21/98	1135		✓
		5/22/98	0940		

LOG BOOK

Project: Ethoprop Ambient in Siskiyou Co.

Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by	
107	BLANK	5/21/88	0435	TAKEN AT LAV SITE		LJ
108	LAV 16	5-26	1320		o	MA
		5-27	1245			
109	NEW 16	5-26	1425			
		5-27	1240			
110	TLB 16	5-26	1500			
		5-27	1410			
111	DOR 16	5-26	1545			
		5-27	1510			
112	MAC 16	5-26	1615			
		5-27	1545			
113	LAV 17	5-27	1245			
		5-28	1100			
114	NEW 17	5-27	1340			
		5-28	1140			
115	TLB 17	5-27	1410			
		5-28	1205			
116	DOR 17	5-27	1510			
		5-28	1250			
117	MAC 17	5-27	1545			
		5-28	1325			
118	LAV 18	5-28	1100			
		5-29	0940			
119	LAV 18D	5-28	1100			
		5-29	0940			
120	NEW 18	5-28	1140			
		5-29	1040			
121	NEW 18D	5-28	1145			
		5-29	1040			
122	TLB 18	5-28	1205			
		5-29	1110			
123	TLB 18D	5-28	1205			
		5-29	1110			
124	DOR 18	5-28	1250			
		5-29	1155			
125	DOR 18D	5-28	1250			
		5-29	1155			
126	MAC 18	5-28	1325			
		5-29	1220			
127	MAC 18D	5-28	1325			
		5-29	1220			
128	LAV 19	5-29	0940		✓	✓
		5-30	0845			

LOG BOOK

Project: Ethoprop Ambient in Siskiyou Co.

Project #: C98-006

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
129	NEW 19	5/29 5/30	1040 0935		o	MAH
130	TLB 19	5/29 5/30	1110 1005			
131	DOR 19	5-29 5-30	1155 1045			
132	MAC 19	5-29 5-30	1220 1115			
133	LAU 20	5-30 5-31	0845 0820			
134	NEW 20	5-30 5-31	0935 0910			
135	TLB 20	5-30 5-31	1005 0935			
136	DOR 20	5-30 5-31	1045 1010			
137	MAC 20	5-30 5-31	1115 1050		↓	
138	LAU 21	5-31 6-1	0820 0815		PC	
139	NEW 21	5-31 6-1	0910 0905			
140	TLB 21	5-31 6-1	0935 0940			
141	DOR 21	5-31 6-1	1010 1015			
142	MAC 21	5-31 6-1	1050 1050			
143	LAU 22	6-1 6-2	0815 0800			
144	LAU 22D	6-1 6-2	0815 0800			
145	NEW 22	6-1 6-2	0905 0845			
146	NEW 22D	6-1 6-2	0905 0845			
147	TLB 22	6-1 6-2	0940 0900			
148	TLB 22D	6-1 6-2	0940 0900			
149	DOR 22	6-1 6-2	1015 0945			
150	DOR 22D	6-1 6-2	1015 0945		↓	↓

Project: Ethoprop Ambient in Siskiyou Co.
Project #: C98-006

74

1st EFTAM start - 0500
MCLAD start 0835
End 1500

2nd start 0650
End

LOG BOOK

Project: Ethoprop Application in Siskiyou Co.
Project #: C98-005

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by	
1	ETH-WB	5/11	1645		O	KEY
		5/12	0830			
2	WFS1	5/11	1645			
		5/12	0830			
3	SB	5/11	1655			
		5/12	0820			
4	SFS2	5/11	1655	Pump/battery died dead over night		
		5/12	0820			
5	EB	5/11	1700			
		5/12	0815			
6	EFS3	5/11	1700			
		5/12	0815			
7	NB	5/11	1710		↓	↓
		5/12	0835			
8	E1	5/12	0815			
		5/12	2010			
9	E1K	5/12	0815			
		5/12	2010			
10	S1	5/12	0820			
		5/12	2015			
11	W1	5/12	0830			
		5/12	2020			
12	N1	5/12	0835			
		5/12	2030			
13	E2	5/12	2010		PC	
		5/12	2340			
14	E20	5/12	2010			
		5/12	2340			
15	S2	5/12	2015			
		5/12	2340			
16	W2	5/12	2020			
		5/12	2345			
17	N2	5/12	2030		↓	↓
		5/12	2350			
18	E3	5/12	2340			
		5/13	0635			
19	E3D	5/12	2340			
		5/13	0635			
20	S3	5/12	2340			
		5/13	0645			
21	W3	5/12	2345			
		5/13	0650			
22	N3	5/12	2350			↓
		5/13	0655			

LOG BOOK

Project: Ethoprop Application in Siskiyou Co.
Project #: C98-005

Log #	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear taken by	
23	E4	5/13	0635		pc	KEM
		5/13	1455			
24	E4D	5/13	0635			
		5/13	1455			
25	S4	5/13	0645			
		5/13	1455			
26	W4	5/13	0650			
		5/13	1500			
27	N4	5/13	0655			
		5/13	1505			
28	E5	5/13	1455			
		5/14	1305			
29	E5D	5/13	1455			
		5/14	1305			
30	S5	5/13	1455			
		5/14	1305			
31	W5	5/13	1500			
		5/14	1300			
32	N5	5/13	1505			
		5/14	1310			
33	E6	5/14	1305			
		5/15	1110			
34	E6D	5/14	1305			
		5/15	1110			
35	S6	5/14	1305			
		5/15	1110			
36	N6	5/14	1300			
		5/15	1100			
37	N6	5/14	1310			
		5/15	1115			
38	Blank	5/15	1045			
39	TS1	5/15	1045	Trip Spike		
40	TS2	5/15	1045			
41	TS3	5/15	1045			

APPENDIX VI

ETHOPROP APPLICATION METEOROLOGICAL DATA

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	131	1644	8.7	48.2	861	59.2	188.2
1998	131	1659	10.2	47.7	861	63.0	213.4
1998	131	1714	9.2	46.4	861	64.7	235.6
1998	131	1729	5.2	46.4	861	66.6	244.7
1998	131	1744	2.6	45.3	860	71.3	237.5
1998	131	1759	1.5	45.1	860	71.7	163.1
1998	131	1814	3.8	45.1	860	77.4	198.6
1998	131	1829	6.1	44.4	860	79.2	193.6
1998	131	1844	1.7	44.2	860	81.4	195.7
1998	131	1859	3.0	43.9	860	82.3	184.8
1998	131	1914	3.1	43.7	860	82.8	197.1
1998	131	1929	0.0	43.6	860	83.0	216.6
1998	131	1944	0.0	43.2	860	81.7	152.8
1998	131	1959	0.0	42.9	860	79.0	114.4
1998	131	2014	0.0	42.9	859	76.2	109.6
1998	131	2029	0.1	42.8	859	75.7	170.3
1998	131	2044	0.0	42.6	859	75.7	149.0
1998	131	2059	0.0	41.8	859	78.2	168.3
1998	131	2114	0.0	41.5	859	78.7	127.6
1998	131	2129	3.4	41.3	859	80.3	154.4
1998	131	2144	6.3	40.9	859	80.4	175.3
1998	131	2159	6.1	40.7	859	82.2	170.5
1998	131	2214	3.8	40.3	859	83.3	180.8
1998	131	2229	4.3	40.3	859	83.6	184.9
1998	131	2244	4.4	40.0	859	86.5	208.5
1998	131	2259	4.9	39.7	858	88.5	215.8
1998	131	2314	5.6	39.6	858	86.3	206.6
1998	131	2329	3.2	39.4	858	85.9	184.4
1998	131	2344	5.4	39.5	858	85.9	197.0
1998	131	2359	5.2	39.2	858	87.6	192.6
1998	132	14	5.2	39.1	858	88.2	199.5
1998	132	29	4.3	39.0	858	89.0	203.0
1998	132	44	4.9	38.8	858	87.1	200.1
1998	132	59	5.4	38.5	858	87.1	188.8
1998	132	114	5.0	38.3	858	87.6	168.6
1998	132	129	2.5	38.1	858	89.3	170.2
1998	132	144	3.6	38.0	858	90.7	179.0
1998	132	159	3.9	38.0	858	91.4	185.4
1998	132	214	2.6	38.1	858	91.1	197.0
1998	132	229	0.9	38.1	858	91.0	226.1
1998	132	244	1.3	37.9	857	92.6	209.5
1998	132	259	2.7	37.7	857	94.5	204.2
1998	132	314	0.7	37.4	857	95.2	202.3

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	132	329	0.2	37.2	857	95.6	194.9
1998	132	344	0.1	37.0	857	97.0	255.5
1998	132	359	0.1	36.3	857	98.7	276.3
1998	132	414	1.2	35.9	857	99.7	262.9
1998	132	429	3.1	35.7	857	99.7	250.1
1998	132	444	1.8	35.4	857	99.7	126.5
1998	132	459	1.6	35.4	857	99.7	88.6
1998	132	514	1.2	35.2	857	99.7	22.1
1998	132	529	0.0	35.0	857	99.7	14.4
1998	132	544	0.0	34.8	857	99.7	22.6
1998	132	559	0.0	34.8	857	99.7	32.5
1998	132	614	0.0	34.9	857	99.7	59.1
1998	132	629	0.0	35.0	857	99.7	80.8
1998	132	644	0.0	35.4	857	99.7	148.9
1998	132	659	0.0	35.9	857	99.7	140.0
1998	132	714	0.0	36.6	857	99.7	152.2
1998	132	729	0.0	37.2	857	99.7	134.9
1998	132	744	0.0	37.8	857	99.7	130.5
1998	132	759	0.0	38.7	857	97.7	190.9
1998	132	814	0.1	40.1	857	92.5	247.3
1998	132	829	0.0	40.9	857	90.0	253.5
1998	132	844	0.0	41.3	857	85.0	210.9
1998	132	859	0.0	42.1	857	84.3	143.3
1998	132	914	0.2	41.9	857	80.1	228.3
1998	132	929	0.1	44.4	857	77.4	140.4
1998	132	944	0.0	45.2	857	72.9	151.5
1998	132	959	1.7	43.0	857	69.4	143.3
1998	132	1014	1.0	42.5	857	71.3	249.4
1998	132	1029	0.7	42.5	857	72.4	319.7
1998	132	1044	0.0	44.2	857	70.6	208.6
1998	132	1059	1.8	44.2	857	69.2	268.8
1998	132	1114	1.5	44.8	857	71.2	197.8
1998	132	1129	0.9	45.1	857	72.7	65.9
1998	132	1144	0.0	47.6	857	69.8	187.8
1998	132	1159	1.0	49.7	857	63.1	159.1
1998	132	1214	5.6	46.5	857	64.3	60.1
1998	132	1229	3.8	46.7	857	66.7	111.7
1998	132	1244	2.8	47.5	857	66.9	76.4
1998	132	1259	1.4	49.3	857	59.1	78.6
1998	132	1314	2.0	48.7	857	58.2	62.9
1998	132	1329	0.4	49.4	857	56.2	115.4
1998	132	1344	3.6	49.3	857	53.3	195.8
1998	132	1359	0.9	49.3	857	51.7	190.1

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	132	1414	0.9	49.6	857	52.3	137.2
1998	132	1429	2.2	48.4	857	53.5	108.2
1998	132	1444	4.1	48.2	857	60.1	92.9
1998	132	1459	7.6	48.4	857	65.3	89.8
1998	132	1514	4.1	50.7	857	61.1	83.8
1998	132	1529	3.1	50.0	857	55.1	177.0
1998	132	1544	8.2	49.2	857	57.6	219.8
1998	132	1559	9.9	49.4	857	63.2	194.0
1998	132	1614	8.6	52.2	857	58.4	207.5
1998	132	1629	8.0	51.8	857	53.9	194.5
1998	132	1644	6.7	51.2	857	54.4	230.9
1998	132	1659	11.9	48.8	857	60.8	316.1
1998	132	1714	11.5	48.7	857	68.3	299.6
1998	132	1729	11.8	47.7	857	68.3	279.8
1998	132	1744	11.3	46.9	857	70.5	308.2
1998	132	1759	9.6	46.8	857	74.5	241.8
1998	132	1814	8.7	47.0	857	76.6	280.4
1998	132	1829	9.2	46.9	857	70.3	333.5
1998	132	1844	10.1	46.4	857	72.1	338.1
1998	132	1859	9.8	45.9	857	72.8	335.1
1998	132	1914	10.5	44.8	857	74.6	336.1
1998	132	1929	8.2	45.0	857	78.0	340.9
1998	132	1944	7.5	44.9	857	77.7	333.0
1998	132	1959	9.6	43.9	858	76.8	321.4
1998	132	2014	9.6	42.1	858	77.6	325.5
1998	132	2029	8.5	41.4	858	79.2	322.0
1998	132	2044	6.9	40.6	858	81.4	326.6
1998	132	2059	5.6	40.0	858	82.4	332.7
1998	132	2114	1.0	38.3	859	84.5	121.4
1998	132	2129	0.0	38.2	859	88.6	107.6
1998	132	2144	0.1	38.2	859	89.9	100.8
1998	132	2159	0.0	38.0	859	91.7	113.4
1998	132	2214	0.0	37.2	859	91.6	153.0
1998	132	2229	0.0	36.8	859	93.8	62.4
1998	132	2244	0.2	37.7	859	97.7	26.0
1998	132	2259	2.1	37.6	859	96.7	128.4
1998	132	2314	1.9	36.9	859	95.8	340.8
1998	132	2329	2.2	36.3	859	96.5	343.6
1998	132	2344	0.1	34.9	859	96.1	128.0
1998	132	2359	1.7	36.4	859	99.7	26.4
1998	133	14	0.0	36.4	859	99.7	103.2
1998	133	29	0.0	35.1	859	99.3	50.9
1998	133	44	0.0	34.9	859	99.7	64.2

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	133	59	0.2	34.9	859	99.7	106.9
1998	133	114	0.2	35.2	859	99.7	135.4
1998	133	129	0.0	35.4	859	99.7	158.9
1998	133	144	0.7	36.7	859	99.7	115.0
1998	133	159	1.7	36.8	859	99.7	74.1
1998	133	214	2.1	36.6	859	99.7	73.1
1998	133	229	1.1	37.3	859	99.7	39.2
1998	133	244	0.0	37.1	859	98.7	65.7
1998	133	259	0.0	36.6	859	98.1	218.8
1998	133	314	0.0	36.8	859	99.6	80.2
1998	133	329	0.0	37.4	859	99.7	110.4
1998	133	344	0.0	37.6	860	99.7	258.4
1998	133	359	0.0	37.7	860	98.6	213.1
1998	133	414	0.0	37.8	860	96.7	119.9
1998	133	429	0.5	37.9	860	95.3	326.2
1998	133	444	1.0	37.8	860	94.3	317.5
1998	133	459	0.7	37.4	860	95.4	332.0
1998	133	514	1.4	37.2	860	95.7	334.7
1998	133	529	0.0	36.9	860	95.9	161.1
1998	133	544	0.0	36.6	860	95.9	147.9
1998	133	559	0.0	36.1	860	96.1	201.7
1998	133	614	0.0	36.0	860	98.0	128.2
1998	133	629	0.0	35.8	860	99.7	113.8
1998	133	644	0.0	36.4	860	99.7	71.5
1998	133	659	0.3	37.2	860	99.5	45.7
1998	133	714	0.1	37.9	860	98.7	73.7
1998	133	729	0.0	39.0	861	96.5	99.9
1998	133	744	3.2	39.9	861	91.7	260.2
1998	133	759	8.4	39.4	861	87.4	340.1
1998	133	814	9.4	40.5	861	84.0	332.2
1998	133	829	9.8	40.4	861	78.5	330.1
1998	133	844	9.9	40.9	861	80.6	333.3
1998	133	859	11.3	42.7	861	75.1	325.4
1998	133	914	11.2	42.5	861	72.9	332.1
1998	133	929	11.1	42.9	861	69.1	326.1
1998	133	944	11.6	44.0	861	66.8	331.2
1998	133	959	11.1	44.4	861	64.1	324.2
1998	133	1014	9.5	44.0	861	62.3	329.9
1998	133	1029	10.3	44.6	861	62.4	319.5
1998	133	1044	10.5	44.1	861	64.1	306.7
1998	133	1059	10.5	44.3	862	64.4	304.1
1998	133	1114	12.1	44.8	862	61.7	310.2
1998	133	1129	11.8	45.0	862	63.9	314.5

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	133	1144	12.1	46.3	862	60.3	305.9
1998	133	1159	10.6	46.8	862	56.7	315.1
1998	133	1214	11.0	47.3	862	55.8	315.2
1998	133	1229	12.0	48.7	862	54.4	295.4
1998	133	1244	10.2	48.1	862	52.5	307.5
1998	133	1259	10.0	49.3	862	53.6	311.6
1998	133	1314	10.9	49.1	862	55.2	300.3
1998	133	1329	10.8	48.5	862	56.8	300.6
1998	133	1344	16.5	47.7	862	60.2	312.4
1998	133	1359	16.2	47.9	862	63.4	318.3
1998	133	1414	16.2	47.7	862	63.8	319.9
1998	133	1429	16.0	46.9	863	63.2	307.4
1998	133	1444	14.7	46.7	863	64.3	310.5
1998	133	1459	14.4	47.7	863	63.2	318.9
1998	133	1514	16.7	48.4	863	60.7	310.7
1998	133	1529	17.4	48.9	863	59.8	299.5
1998	133	1544	18.1	48.8	863	60.0	313.1
1998	133	1559	18.3	48.9	863	60.2	301.1
1998	133	1614	17.8	47.7	863	62.7	298.4
1998	133	1629	15.1	47.6	863	64.9	293.1
1998	133	1644	15.8	47.5	863	63.9	304.1
1998	133	1659	17.5	47.8	863	64.4	309.1
1998	133	1714	19.3	47.4	863	65.5	308.7
1998	133	1729	21.7	47.3	863	65.2	308.3
1998	133	1744	20.0	47.9	863	66.2	308.5
1998	133	1759	20.1	47.4	864	66.8	308.3
1998	133	1814	17.2	46.3	864	68.9	309.0
1998	133	1829	15.8	45.5	864	71.9	307.8
1998	133	1844	12.0	45.0	864	74.7	313.2
1998	133	1859	11.9	44.5	865	77.2	312.2
1998	133	1914	10.4	44.1	865	78.7	299.6
1998	133	1929	10.4	43.7	865	79.3	302.1
1998	133	1944	7.7	43.7	865	79.8	303.9
1998	133	1959	5.8	43.7	865	80.1	304.3
1998	133	2014	7.9	43.6	865	81.0	304.4
1998	133	2029	12.4	43.4	865	81.4	314.4
1998	133	2044	13.3	43.4	865	82.8	312.4
1998	133	2059	7.2	43.3	865	84.4	310.2
1998	133	2114	5.3	43.1	866	85.2	312.6
1998	133	2129	3.3	43.2	866	85.4	308.4
1998	133	2144	6.7	43.3	866	85.6	304.3
1998	133	2159	6.3	43.4	866	85.7	303.7
1998	133	2214	6.3	43.3	866	86.2	301.8

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	133	2229	4.0	43.2	866	87.2	301.7
1998	133	2244	3.7	43.2	866	88.2	299.8
1998	133	2259	2.3	43.2	866	89.0	304.9
1998	133	2314	3.9	43.2	866	90.0	305.0
1998	133	2329	0.6	42.6	866	93.0	174.2
1998	133	2344	1.5	42.5	866	94.0	163.6
1998	133	2359	0.0	42.0	866	96.7	196.8
1998	134	14	0.0	42.3	866	96.1	139.2
1998	134	29	0.0	42.4	866	97.4	184.8
1998	134	44	0.0	42.7	866	95.9	179.8
1998	134	59	1.0	43.2	866	92.3	304.8
1998	134	114	2.1	43.2	866	91.7	283.7
1998	134	129	4.9	43.5	866	89.6	294.6
1998	134	144	0.1	43.2	866	90.2	275.1
1998	134	159	1.3	43.4	866	89.1	278.2
1998	134	214	0.4	43.1	866	90.4	310.9
1998	134	229	0.0	42.7	866	91.7	281.7
1998	134	244	2.4	42.6	866	93.3	298.7
1998	134	259	5.6	42.4	866	94.5	305.1
1998	134	314	5.8	42.2	866	95.9	307.2
1998	134	329	5.3	42.1	866	95.8	302.2
1998	134	344	5.8	41.9	866	95.7	313.4
1998	134	359	4.4	41.7	866	96.5	314.2
1998	134	414	1.3	41.4	866	97.5	332.7
1998	134	429	0.0	41.4	866	97.7	290.2
1998	134	444	0.1	41.5	866	96.2	328.0
1998	134	459	0.2	41.4	866	95.9	329.1
1998	134	514	2.2	41.2	866	96.0	327.8
1998	134	529	3.9	41.1	866	95.6	314.9
1998	134	544	4.8	40.9	866	96.3	315.5
1998	134	559	2.0	40.6	866	98.1	327.7
1998	134	614	0.2	40.6	866	98.9	317.2
1998	134	629	1.3	41.0	866	98.7	310.9
1998	134	644	0.5	41.3	866	97.9	313.6
1998	134	659	3.4	41.4	866	95.4	300.8
1998	134	714	2.0	41.5	866	93.8	298.5
1998	134	729	0.0	42.2	866	93.8	270.4
1998	134	744	2.6	42.3	866	90.8	325.9
1998	134	759	1.9	42.6	866	88.6	318.2
1998	134	814	2.4	42.8	866	87.5	316.6
1998	134	829	0.6	44.0	867	86.2	212.3
1998	134	844	0.2	46.5	867	83.5	169.1
1998	134	859	4.9	45.5	867	76.5	218.1

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	134	914	2.4	47.3	867	75.7	173.5
1998	134	929	7.7	47.6	867	67.0	259.0
1998	134	944	6.5	46.7	867	68.9	278.1
1998	134	959	7.8	47.0	867	70.0	285.3
1998	134	1014	9.1	47.1	867	67.5	271.4
1998	134	1029	10.1	47.2	867	62.5	250.8
1998	134	1044	12.7	46.4	867	65.6	265.0
1998	134	1059	14.1	43.6	867	74.7	316.0
1998	134	1114	11.1	43.1	867	82.5	311.6
1998	134	1129	9.1	43.5	868	81.2	300.8
1998	134	1144	8.4	43.7	868	77.4	263.9
1998	134	1159	6.3	43.9	868	76.7	270.8
1998	134	1214	7.1	45.1	868	72.1	240.8
1998	134	1229	4.6	45.8	868	70.1	250.4
1998	134	1244	5.8	46.3	868	67.9	250.5
1998	134	1259	9.0	46.2	868	69.9	214.1
1998	134	1314	10.8	46.7	868	67.2	234.0
1998	134	1329	11.7	47.1	868	61.7	241.4
1998	134	1344	11.6	47.3	868	63.4	231.3
1998	134	1359	14.5	47.9	868	64.0	234.6
1998	134	1414	15.2	49.1	868	62.4	242.4
1998	134	1429	15.2	49.1	869	59.9	231.5
1998	134	1444	14.3	50.3	868	58.1	227.1
1998	134	1459	15.8	51.3	868	55.5	241.2
1998	134	1514	14.3	50.8	868	56.0	233.7
1998	134	1529	12.9	52.1	868	54.5	231.4
1998	134	1544	13.5	52.0	868	51.3	242.6
1998	134	1559	13.3	51.4	868	52.8	237.0
1998	134	1614	12.2	51.6	868	53.9	240.8
1998	134	1629	11.6	51.3	868	55.6	258.6
1998	134	1644	11.5	51.4	868	55.5	257.1
1998	134	1659	12.2	52.0	868	56.3	240.7
1998	134	1714	15.2	50.9	868	56.3	243.3
1998	134	1729	15.3	50.3	868	58.0	250.1
1998	134	1744	14.1	49.6	869	59.1	275.9
1998	134	1759	10.8	49.5	869	62.4	237.6
1998	134	1814	10.2	49.6	869	62.4	238.1
1998	134	1829	12.6	50.2	869	59.9	262.0
1998	134	1844	14.7	50.8	869	57.1	256.7
1998	134	1859	13.3	50.5	869	55.7	271.3
1998	134	1914	12.3	49.2	869	56.4	268.1
1998	134	1929	10.1	48.1	869	61.1	261.0
1998	134	1944	10.4	47.8	869	64.4	273.0

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	134	1959	12.6	46.3	869	68.9	302.6
1998	134	2014	11.0	45.2	869	72.8	300.6
1998	134	2029	9.5	44.2	869	75.7	299.5
1998	134	2044	9.4	44.1	870	77.4	293.9
1998	134	2059	7.4	44.1	870	77.0	280.1
1998	134	2114	8.2	44.5	870	73.9	266.0
1998	134	2129	5.4	43.5	870	75.5	259.1
1998	134	2144	7.7	43.7	870	77.7	282.8
1998	134	2159	4.2	43.1	870	78.8	272.5
1998	134	2214	0.0	40.3	870	79.0	142.2
1998	134	2229	0.4	41.3	871	83.9	148.2
1998	134	2244	0.1	42.5	870	84.4	249.6
1998	134	2259	1.8	42.5	870	84.0	277.0
1998	134	2314	1.2	41.8	870	83.6	270.4
1998	134	2329	0.0	40.7	870	84.8	272.7
1998	134	2344	0.1	40.0	870	87.2	100.0
1998	134	2359	0.1	41.2	870	88.4	132.2
1998	135	14	0.6	41.7	870	88.6	176.8
1998	135	29	0.0	41.6	870	88.2	204.9
1998	135	44	0.1	42.0	870	87.3	321.1
1998	135	59	2.1	41.5	870	88.4	325.9
1998	135	114	0.1	41.4	870	88.7	318.4
1998	135	129	0.1	41.4	870	88.1	317.5
1998	135	144	0.1	41.1	870	88.9	333.9
1998	135	159	2.5	41.0	870	88.7	311.7
1998	135	214	2.9	40.8	870	89.1	332.6
1998	135	229	4.6	40.6	870	90.8	319.4
1998	135	244	4.2	40.8	870	90.6	307.6
1998	135	259	2.4	40.2	870	90.7	323.5
1998	135	314	3.5	39.6	870	91.5	314.3
1998	135	329	2.3	39.2	870	92.7	326.1
1998	135	344	0.8	38.9	870	95.0	221.6
1998	135	359	1.8	38.4	870	95.9	129.2
1998	135	414	2.9	37.7	870	98.2	35.4
1998	135	429	3.3	37.5	870	99.7	219.0
1998	135	444	1.1	37.7	870	99.7	345.6
1998	135	459	5.7	37.3	870	98.6	320.8
1998	135	514	5.1	36.6	871	97.4	336.9
1998	135	529	1.2	36.1	871	99.6	133.7
1998	135	544	1.4	35.2	871	99.7	42.8
1998	135	559	1.7	35.1	871	99.7	28.1
1998	135	614	2.0	35.3	871	99.7	36.3
1998	135	629	0.6	35.5	871	99.7	52.2

ETHOPROP APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temperature (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction
1998	135	644	3.1	35.5	871	99.7	39.8
1998	135	659	2.7	35.4	871	99.7	46.7
1998	135	714	2.9	35.6	871	99.7	30.1
1998	135	729	4.1	36.0	871	99.7	80.0
1998	135	744	5.3	36.2	871	99.3	168.2
1998	135	759	5.3	36.5	871	99.0	81.1
1998	135	814	4.8	37.3	871	97.6	24.0
1998	135	829	5.2	37.5	871	94.2	238.8
1998	135	844	3.9	37.5	871	93.4	125.5
1998	135	859	2.3	38.1	871	94.2	128.7
1998	135	914	2.5	37.9	871	93.1	47.5
1998	135	929	2.5	38.2	871	93.3	45.5
1998	135	944	2.5	39.6	871	93.9	125.0
1998	135	959	1.8	41.3	871	88.1	225.7
1998	135	1014	1.1	42.8	871	83.2	201.8
1998	135	1029	4.0	41.9	871	79.1	325.3
1998	135	1044	2.1	43.4	871	76.6	185.4